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# CYSENI 2021

## **Dear Colleagues,**

The International Conference of Young Scientists on Energy and Natural Sciences Issues (CYSENI 2021) has been organized already for the 17th time since 2004, which became an annual tradition. We are very proud to bring together talented young scientists to participate in the 17th CYSENI conference. We expect that this will contribute to exchange of ideas, improved knowledge of young researchers, development of their acquired abilities and contribute to increasing level of exercised research activities. The initiative for such an event came from young and enthusiastic researchers of Lithuanian Energy Institute (LEI). They realised that there are a lot of young, smart and science-oriented young people and they do need a place to share their views, generated ideas and present the latest research results.

This year, for the first time in the history of the CYSENI conference, the event was held online. Due to the challenges of the epidemiological situation, the organizers sought new solutions: the new website was launched and adapted to accommodate an online format.

However, the challenges had also led to many positive changes. Through RTO Lithuania – an association of non-university research and technology organizations, we, the Lithuanian Energy Institute, the Lithuanian Research Centre for Agriculture and Forestry as well as the Center for Physical Sciences and Technology established a partnership in co-organizing the CYSENI conference. This partnership allowed us to expand the topics of the conference and it seems like all of our work has paid off because this year, we had a record-high number of presentations – 178 by 173 participants from 29 countries!

The conference once again has brought together young researchers and scientists to discuss recent trends in energy and natural sciences sectors worldwide. We are pleased that young scientists further found the conference valuable to present their up-to-date research results and share scientific experience.

We thank all the contributors who made this conference possible. This includes all people from scientific and organising committees. We would like to thank all participants for their contributions to the Conference and submission of their research papers. Moreover, special thanks to Keynote speakers - Bogdan Voisiat, Zigmas Balevičius, Ana Luisa Fernando, Paula Peiró García, Tomi J. Lindroos, Roman Antipenkov and Erik Kjellström.

Sincerely,

**Conference Organizers** 

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# **PLENARY SPEAKERS**

#### BOGDAN VOISIAT SENIOR RESEARCH SCIENTIST AT DRESDEN UNIVERSITY OF TECHNOLOGY, GERMANY:

Direct laser interference patterning: from basics to industrial applications

# ZIGMAS BALEVIČIUS

HEAD OF PLASMONICS AND NANOPHOTONICS LABORATORY AND CHIEF RESEARCHER AT CENTER FOR PHYSICAL SCIENCES AND TECHNOLOGY, LITHUANIA:

Plasmonics: from biosensing to nanolasers

### ANA LUISA FERNANDO

ASSOCIATE PROFESSOR AT UNIVERSIDADE NOVA DE LISBOA, PORTUGAL: Cultivation of energy crops in marginal soils – technological, environmental, social and economic opportunities and risks

## PAULA PEIRÓ GARCÍA

EXECUTIVE COORDINATOR OF H2020 AURORAL PROJECT, SPAIN: Smarter Communities, a new paradigm for Europe

## TOMI J. LINDROOS

SENIOR SCIENTIST AT VTT TECHNICAL RESEARCH CENTER, FINLAND: Decarbonization and electrification in Baltic countries and Northern Europe

#### ROMAN ANTIPENKOV

DEPUTY HEAD OF THE ALLEGRA LASER DEVELOPMENT GROUP AT ELI-BEAMLINES, CZECH REPUBLIC: Advanced Laser Systems at ELI Beamlines Facility: from 3 TW to 10 PW

## ERIK KJELLSTRÖM

PROFESSOR AT SWEDISH METEOROLOGICAL AND HYDROLOGICAL INSTITUTE, SWEDEN:

Climate modelling in support of adapting the energy sector for future climate conditions in Northern Europe



# **BOGDAN VOISIAT** SENIOR RESEARCH SCIENTIST AT DRESDEN UNIVERSITY OF TECHNOLOGY, GERMANY

# Direct laser interference patterning: from basics to industrial applications

Surface structuring has attracted significant attention due to the rising need of the industrial sector to improve their products through surface functionalization. An up-and-coming technology for this purpose is based on laser material processing called Direct Laser Interaction Patterning (DLIP). It implements interference of multiple laser beams to form periodical patterns with a single laser pulse directly. This provides the ability to utilize the total laser power for high-speed structuring of large surface areas. However, in some cases, even higher speeds are required. Therefore, alternative technologies like roll-to-roll hot embossing must be utilized. By the synergy of the DLIP technology, which is used for structuring the sleeves (embossing tool) and the roll-to-roll hot-embossing method, the throughput for the fabrication of micro/nanostructured polymer foils can be increased at least one order of magnitude. Furthermore, since the sleeves are processed directly, without lithographic methods, the fabrication cost of the textured drums can be significantly reduced (up to ~ 90%).

In this talk, the introduction to the Direct Laser Interference Patterning technology is provided. The key features that give the rising popularity to this process will be discussed. Moreover, the most interesting applications where DLIP can be implemented are presented, and the future outlook to the industrial applications is revealed.



# PAULA PEIRÓ GARCÍA EXECUTIVE COORDINATOR OF H2020 AURORAL PROJECT, SPAIN

# Smarter Communities, a new paradigm for Europe

The smart community concept is new and evolving as the number of communities using "smart" technologies continues to grow. This concept is embedded in the H2020 AURORAL project, which focuses on increasing connectivity and delivering a digital environment of smart objects interoperable services platforms able to trigger dynamic rural ecosystems of innovation chains, applications and services. AURORAL digital environment is demonstrated by cost-efficient and flexible cross-domain applications through large-scale pilots in five European regions. It builds on an open, API-based, interoperable and federated Internet of Things (IoT) architecture and includes a reference implementation supporting flexible integration of heterogeneous services, bridging the interoperability gap of the smart object platforms and creating markets for services in rural areas. AURORAL has the potential to shape the on-going discussion about the "Smart Community" approach as it provides a methodological framework needed to address one of the main challenges embedded in the Smart Villages approach, the lack of digital infrastructure. AURORAL opens to every European rural region the access to state-of-the-art digital capabilities and the impacts of those capabilities on regional innovation.



# **TOMI J. LINDROOS** SENIOR SCIENTIST AT VTT TECHNICAL RESEARCH CENTER, FINLAND

# Decarbonization and electrification in Baltic countries and Northern Europe

The EU commission is suggesting a significant increase to the ambition level of 2030 energy and climate policies to stay on path to carbon neutrality at 2050. At the same time, wind power, solar power, electric vehicles, and heat pumps have developed significantly faster than assumed in many previous modelling studies. Wind and solar, depending on region, are becoming cheaper than existing fossil-based capacity, but their variability and acceptability might increase the costs or limit the build-out. Northern Europe has a high share of combined heat and power (CPH), but current market situation sees fossil CHPs replaced by biomass CHP, biomass heat only boilers, or large heat pumps, depending on local policies and resources. Buildings has been one of most rapidly decarbonizing sectors in the EU as fossil fuels are relatively easy to replace with solar PVs or heat pumps. However, these technologies might have limited production during the winter creating additional peak demand to the grid. Seasonal energy storages would solve many of these issues, but reservoir hydro is still the only commercial option in a very-large-scale storages. Transport and industry need clean electricity and heat either directly or as fuels to replace fossil fuels. Direct electrification of personal transportation (electric vehicles, EVs) seems to be a key technology and EVs are reaching the cost parity over the vehicle lifetime with gasoline and diesel vehicles during 2020's. Upfront costs of EVs might still be an issue, but European countries are increasing taxes of even planning restrictions on fossil vehicles. Heavy transport and industry are the most difficult energy sectors to decarbonize and current technology options include direct electrification, CCS, and P2X. The studied applications vary from sector to sector and upcoming large-scale demonstrations need to show the feasibility of these solutions.



# **ROMAN ANTIPENKOV**

DEPUTY HEAD OF THE ALLEGRA LASER DEVELOPMENT GROUP AT ELI-BEAMLINES, CZECH REPUBLIC

# Advanced Laser Systems at ELI Beamlines Facility: from 3 TW to 10 PW

ELI-Beamlines facility together with ELI-ALPS and ELI-NP are the three pillars of ELI project, aimed at enabling unique research capabilities for international users. All three facilities have state-of-the-art laser systems and secondary radiation sources, which are being used for novel scientific experiments. ELI-Beamlines hosts four one-of-a-kind laser systems, ranging with energies from tens of millijoules at 1 kHz repetition rate to kilojoule energy per single shot every minute. Additionally, there are several support lasers installed, which allows to commission the technology and prepare for high-energy experiments in parallel with the main laser system servicing and development. A unique feature of ELI-Beamlines is a potential ability to synchronize the outputs from separate petawatt lasers with different parameters and use them in the same experiment. Currently, most of the main technologies have been verified and the laser teams are working on ramping up the performance of the laser systems to their nominal level while at the same time performing pilot experiments in the X-ray generation or particle acceleration fields.

In this talk, the current state of the laser systems in ELI-Beamlines as well as technology and innovations behind this development are presented. Also, some of the applications and on-going research are covered briefly.



# **ERIK KJELLSTRÖM** PROFESSOR AT SWEDISH METEOROLOGICAL AND HYDROLOGICAL INSTITUTE, SWEDEN

# Climate modelling in support of adapting the energy sector for future climate conditions in Northern Europe

Ongoing climate change is rapid. For Northern Europe, shorter and milder winters and longer and warmer summers are already observed. Future climate change is unavoidable although the degree of change is not known as it strongly depends on future emissions of greenhouse gases. A prominent way of reducing emissions is a shift from fossil-fuel energy sources to renewable energy. The systems that will provide such energy in the future will be operated in the future climate. Therefore, it may not be adequate to plan and design these systems solely based on historical climate information from observations. In this presentation I will talk about the application of a large ensemble of regional climate model projections for Europe. A range of indices of relevance for the energy sector has been computed based on these projections for a number of different future warming levels, i.e. 1.5, 2, 2.5, etc. degrees global warming with respect to pre-industrial conditions. Changes at these future warming levels relative to the historical climate will be presented. The results show continued warming, shifting of seasons, an intensified hydrological cycle all with potential impacts on the energy sector both in terms of energy production and energy demand. Changes in the wind climate are more uncertain as are many changes in extreme conditions, partly due to limitations in data availability and climate model resolution.

# **ZIGMAS BALEVIČIUS** HEAD OF PLASMONICS AND NANOPHOTONICS LABORATORY AND CHIEF RESEARCHER AT CENTER FOR PHYSICAL SCIENCES AND TECHNOLOGY, LITHUANIA

# Plasmonics: from biosensing to nanolasers

Presentation is dedicated to the phenomenon of surface plasmon resonance and it's applications in the field of optical biosensing, tunable photonic devices and plasmonic based nanolasers. Various types of plasmonic excitation will be presented and their optical properties discussed. Special attention will be paid for the reduction of losses in the hybrid plasmonic modes. The examples of employing plasmonic phenomenon for the detection of proteins interactions such as SARS-COVID-2, granulocyte colony stimulating factor receptor (GCSF-R) and others will be presented. Also, potential applications of plasmonics based nanostructures for the new type of the coherent light sources will be discussed.



# ANA LUISA FERNANDO ASSOCIATE PROFESSOR AT UNIVERSIDADE NOVA DE LISBOA, PORTUGAL

# Cultivation of energy crops in marginal soils – technological, environmental, social and economic opportunities and risks

An increasing global awareness that the supply and security of petroleum-based materials is diminishing, coupled with environmental concerns related to climate change, has increased demand for more renewable, diversified, and sustainable systems. Energy crops are promising resources which can replace products and materials of fossil origin. Yet, the increasing demand for biomass may increase the risk of conflicts on land use due to competition for food and feed. Hence, segregating the growth of dedicated biomass crops on marginal land is considered a potential option to avoid these conflicts. Studies on the production of energy crops in marginal soils have been reviewed, taking into account environmental, economic and socio-economic aspects as also the technological obstacles associated with biomass characteristics and opportunities and risks will be pointed out.

# **CONFERENCE PAPERS**

# I. ENERGY SCIENCES

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#### OBSERVED AND PROJECTED TRENDS OF NEAR-SURFACE WIND SPEED IN LITHUANIA FOR ENERGY APPLICATIONS

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#### EXTENDED ABSTRACT

#### **OVERVIEW**

The development of a wind farm usually starts with an accurate analysis of the wind efficiency in a given area. Recent studies show that wind speeds are changing, especially when considering the timeframe required for wind farm projects. This study analyses the observed and projected long-term (up to 2100) changes of the near-surface (or 10 m) wind speed in Lithuania. This study analyses daily wind speed observations measured at Lithuanian Hydrometeorological stations between 2006 and 2019. The predicted wind speeds are based on the results of 3 Global Circulation Models for the following scenarios: RCP2.6, RCP4.5 and RCP8.5.

#### **METHODS**

The National Oceanic and Atmospheric Administration (NOAA) provided the historical wind speed data [1]. Wind speed data are recorded from 1901 to 2020, although many data points are missing in the early years. In this study, historical wind speed data has been used from 2006 until 2020 as the reference period (RF). Projected wind speed assessment has been performed using three RCP scenarios: the mildest RCP2.6, the most realistic RCP4.5 and the most severe RCP8.5. The data has been taken from IPCC Distribution Center [2], [3], extracted and downscaled. Three Global Circulation Models (GCMs) were used in this research: MPI-ESM-LR (Max Planck Institute for Meteorology Earth System, further MPI), HadGEM2-ES (the Hadley Centre Global Environmental Model, further HAD), IPSL-CM5A-MR (Institute Pierre Simon Laplace, further IPSL). The analysis of meteorological data was carried out in two ways. In the first case, all three models (IPSL, MPI and HAD) were averaged and wind speed analysis was performed. In the second case, the country was divided into four regions: coastal, northern, central, and southern. The average wind speed for each region was analysed for each model and scenario separately. In both cases, the 21st century was divided into three periods: the near future (2020 - 2040), the middle future (2040 - 2060) and the far future (2080 - 2100).

#### RESULTS

The projected changes in wind speed were analysed using three models, which were averaged into one and three scenarios: the mildest RCP2.6, the most likely RCP4.5 and the most severe RCP8.5. The results of the analysis for the near future are presented in Fig. 1 as a map of the wind speed change. Based on the results of the RCP2.6 and RCP8.5 scenario analyses, the wind speed change across the whole territory of Lithuania will vary between 0 % and 2 % in the near future (2020 - 2040). Meanwhile, the most likely scenario shows a significant decrease in wind speeds, which could reach up to 6 % in most of the country. A decrease in wind speed is expected under the RCP4.5 and RCP8.5 scenarios of up to 2 % and 6 % respectively in the middle future. In the mildest scenario (RCP2.6), wind speeds are expected to increase by up to 3 % in the distant future (2080 - 2100) across the country. The analysis of the most realistic projection shows a possible decrease in wind speed of up to 8.2 %. The average national wind speed reduction could be around 6 % under the RCP4.5 scenario. In the most pessimistic scenario (RCP8.5), wind speeds would also decrease, but reduction should be less than 2.5 %.



Fig. 1. Wind speed change in Lithuania under various scenarios in the near future (2020 - 2040).

The regional analysis shows that the mildest scenario RCP2.6 will have little or no negative impact on wind speed change. The highest increase in wind speed might be noticed in the coastal region in the end of the 21st century. Meanwhile, the analysis of the most likely RCP4.5 scenario shows that wind speeds could decline significantly. For example, according to the HAD model, wind speeds in central Lithuania can be expected to decrease by up to 30 %. Even though RCP8.5 is generally considered to be the most unfavourable scenario, the analysis shows that this scenario should not lead to such a significant reduction in wind speed as RCP4.5. Wind speed should remain the same as in the reference period for all models except HAD in all regions. HAD model shows strong wind speed reduction in northern, southern, and central regions. The decline may reach up to 20 %. The coastal region is the only region in Lithuania where an increase in wind speed is expected under any scenario and model.

#### CONCLUSIONS

This study analysed the projected changes in wind speed in the 21st century. The mildest scenario, RCP2.6, was found to have a positive impact on wind speed trends. Average wind speeds are expected to remain constant or increase slightly (up to 3% in the far future). In contrast, the most realistic scenario RCP4.5 is likely to have the strongest negative impact. The regional analysis of the models shows a potential wind reduction of up to 30 %. The most severe scenario, RCP8.5, is unlikely to have as strong a negative impact on wind speed trends as RCP4.5.

Keywords: climate change, wind speed, projections, RCP scenarios

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#### NEW WAY TO USE CONCENTRATED SOLAR HEATING: DESIGN OF AN INTEGRATED SOLAR BOILER

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#### ABSTRACT

*IPCC* (*Intergovernmental Panel on Climate Change*) recommends in order to avoid global warming over  $1.5^{\circ}$ C to reach net-zero of  $CO_2$  emission by 2050. But in 2018 the global primary energy consumption mix included 27% of coal, 24% of Natural gas, and 34% of Oil. The high percentage of using non sustainable fuel sources highlights the importance of reducing the use of fossil fuels in almost all human activities. Steam boilers, the concentration of chemical products, and desalination are among the examples where boiling is required in industrial processes. The fuel used in these boilers is generally fossil fuel.

In this context, a new solar boiler is studied which operates under different boiling regimes with concentrated solar energy. Such solar energy is provided by a heliostat which concentrates the direct solar radiation on a small boiling module. As a result of that the boiler is heated and produces the steam which is extracted from the above.

This Paper proposes a modelling approach, to adjust the use of the concentrated solar boiler to increase the thermal efficiency of the boiler. The model is capable of describing boiling at different temperatures under concentrated solar heating. Many application fields, like desalination, perform boiling on a scaling liquid. This is the reason why the film boiling regime at higher temperatures is important to take into consideration. Under this boiling condition, a thin vapor layer is formed between the receiver and the liquid and the contact between the surface of solar the receiver and the liquid can be avoided to improve the equipment's lifetime. The thermal efficiency of the boiler, was 0.934 and 0.781, respectively in nucleate and film boiling. A 200 m<sup>2</sup> solar field (mirrors) allowed to reduce the equivalent carbon footprints by 0.281 kg CO<sub>2</sub>-Eq per 1 kWh of steam power produced when replacing a natural gas boiler with a solar boiler.

Keywords: Concentrated solar heating, Solar energy, solar boiler modelling, Boiling

#### INTRODUCTION

Climate change could be one of the most important challenges facing humankind currently and, in the decades, to come. To limit the global rise in temperature below  $1.5^{\circ}$ C above the pre-industrial level, the Intergovernmental Panel on Climate Change (IPCC) recommends reducing emissions of CO<sub>2</sub> by 45% between 2010 and 2030 and reach net-zero by 2050 [1].

The difficulty of reversing the curve of  $CO_2$  emission can be explained by the heavy dependence on fossil fuels as the primary energy consumption mix, 27% of coal, 24% of natural gas, and 34% of oil in 2018 [2]. Also, the distribution of  $CO_2$  emissions in nearly all human activities implies structural changes in all these fields.

In this context, new solutions have to be found and implemented, not only in terms of energy sources but also in their different uses. Solar energy is already well-established renewable energy. For examples the evolution of electricity production with photovoltaics started from 6 GW installations in 2006 up to 505 GW installations in 2018, and that of the CSP (Concentrated Solar Power) from 0.36 to 5.47 GW installed at the same period of time [3].

On an industrial scale, a boiler could be used in the food industry for cooking, distillation, building materials industry, or generally in all chemical industry. The steam production in steam boilers ranges from a few kg.h<sup>-1</sup> to 55 000 kg.h<sup>-1</sup> depending on the scale and use ( $\approx$  38 MW) [4]. The efficiency of a boiler is defined by the ratio between the sensible and latent heat necessary to generate the steam, and the input heating power. In conventional boilers, typical efficiency will depend on the fuel used ( $\approx$ 95% for natural gas, 92-95% for oil, and 88-92% for coal) [5].

Since boilers are wildly used, boiling process have been widely studied for a long time. It is interesting to note that the boiling process can occur in different regimes, depending on the heat flux transmitted to the fluid and the temperature of the hot source in contact with the boiling fluid. (i) For a very small heat flux and low temperatures, natural convection usually occurs, (ii) when heat flux increases together with the hot source temperature, nucleate boiling appears. (iii) When the heat flux becomes too imperative, the liquid cannot access the hot surface because of the vapor formation and a vapor film takes place between the heating surface and the liquid, this boiling regime is called film boiling [6]. Generally, nucleate boiling is preferable compared to film boiling because the heat transfer is much more efficient under these conditions. This work considers both nucleate and film boiling regimes. In fact, for certain boiling fluids with scaling or corrosion problems, such as in desalination, film boiling can be used avoid the direct contact between the fluid and the hot source [7].

#### METHODOLOGY

#### **Integrated solar boiler modelling**

A simple model of a solar boiler has been developed. The solar boiler is composed of (i) a solar field which collects and concentrates solar energy, (ii) a receiver which receives the concentrated solar energy before transmitting it to the boiling fluid, (iii) a tank where boiling takes place as shown in Figure (1).

The solar receiver is defined by its material characteristics, geometries, and thermal properties. Where these parameters are the receiver temperature  $(T_s)$ , the heat exchange surface of the receiver (S), its emissivity ( $\varepsilon_s$ ), its upward view factor (F), and its rugosity for the surface in direct contact with the boiling fluid ( $R_p$ ).





The tank where boiling takes place it is large enough to encapsulated the desired pool boiling. It is also considered as well insulated, Meanwhile the temperature in the tank is equal to the bubble point  $(T_b)$ , determined according to the operating pressure P in the tank. The overall heat balance for water in the tank is given in Equation 1.

$$\dot{m}_{v,out} \cdot (h_{v,out} - h_{l,in}) + \dot{m}_{l,out} \cdot (h_{l,out} - h_{l,in}) = \dot{Q}_b, \tag{1}$$

$$\dot{Q}_b = \dot{Q}_{rad} - \dot{Q}_{loss}.$$
(2)

With  $\dot{m}_{v,out}$ , and  $\dot{m}_{l,out}$  respectively the mass flow rates for the outlet vapor and outlet liquid in kg.s<sup>-1</sup> (the mass balance implies for the inlet mass flow rate  $\dot{m}_{l,in} = \dot{m}_{v,out} + \dot{m}_{l,out}$ ). h<sub>l,in</sub>, h<sub>v,out</sub>, and h<sub>l,out</sub> are the mass enthalpies in J.kg<sup>-1</sup> respectively for the inlet liquid, the saturated vapor, and liquid at the outlet.  $\dot{Q}_b$  (in W) is the boiling heat power effectively transferred to the fluid in the tank,  $\dot{Q}_{rad}$  (in W) the concentrated solar power at the receiver.  $\dot{Q}_{loss}$  (in W) is the power loss from the receiver by radiosity, which is the combination of power emitted by radiation and reflection by the receiver. The calculations of fluid and thermal properties have been carried out using the CoolProp library [8] on Python programming language.

#### Formulation of heat transfer terms

The completion of the heat balance equation requires the knowledge of concentrated solar power at the receiver  $(\dot{Q}_{rad})$ , power loss by radiosity  $(\dot{Q}_{loss})$ , and the temperature at the receiver which depends on the magnitude of boiling heat  $(\dot{Q}_b)$  as well as the geometries of the receiver.

The concentrated solar power  $(\dot{Q}_{solar})$  denotes the radiative solar power reaching the receiver level resulting from the concentration and optical devices beforehand and which depends also on the available Direct Normal Irradiance (DNI). Details of its calculation are given in Section 2.2. The energy losses from the receiver are estimated by following the method proposed by Modest [9]:

$$\dot{Q}_{loss} = \frac{\dot{Q}_{rad} \cdot F.(\frac{1}{\varepsilon_{s}} - 1) + S.F.\sigma_{SB}.T_{s}^{4}}{\frac{1}{\varepsilon_{s}} - (\frac{1}{\varepsilon_{s}} - 1).(1 - F)}.$$
(3)

With  $\dot{Q}_{rad}$  the concentrated solar power at receiver in *W*,  $\varepsilon_s$  the receiver emissivity, S the receiver surface in m<sup>2</sup>,  $\sigma_{SB}$  the Stefan-Boltzmann constant, and F the view factor between the receiver surface and the surrounding.

Depending on the temperature and heat exchange surface of the receiver, two boiling conditions can occur for a given boiling power  $\dot{Q}_b$ : (i) nucleate boiling condition following the correlation of Cooper [10] given in Equation 4, and (ii) film boiling using Equation 5.

$$\dot{Q}_b = S. \left( 55. (P_r)^{0.12 - 0.21 \cdot \log(R_p)} \cdot (-\log(P_r))^{-0.55} \cdot M^{-0.5} \cdot (T_s - T_b) \right)^3, \tag{4}$$

$$\dot{Q}_b = h.S.(T_s - T_b).$$
 (5)

With  $P_r$  the reduced pressure of the fluid ( $P_r = P/P_c$ ),  $R_p$  the rugosity of receiver surface in  $\mu$ m, M the molar mass in g.mol<sup>-1</sup>, and  $T_s$  and  $T_b$  the receiver and boiling temperature in K, respectively. In Equation 5, h is the film boiling heat transfer coefficient involving both conductive and radiative heat transfers, which is estimated using the methodology proposed by Rohsenow et al. [11].

#### Supply of concentrated solar energy

A concentrated solar thermal system can be described by four principal steps illustrated in Figure 2, (i) the collection and concentration of the solar energy through mirrors and reflectors, (ii) the conversion of radiative solar power into thermal power via a receiving system allowing to transfer the heat to a fluid, (iii) the storage of heat using intermediate thermal fluids, and (iv) the conversion of heat to other forms of energy through different thermodynamic cycles. In this context, the boiling is usually carried out at the end, i.e. at the level of thermodynamic cycles, and it is not directly implemented at the level of the solar receiver (Step 2 in Figure 2). Only a few designs study the boiling directly at the receiver level, for instance, the 9 MW linear fresnel installation of Llo (France) [12]. In such a configuration, the storage is made thanks to steam accumulators. One of the principal interests of direct boiling at the solar receiver is to avoid the use of intermediate thermal transfer fluids, which are generally expensive and environmentally harmful.

Here, we are interested in the first step of the collection and concentration of solar energy. Table 1, compares the characteristics, performance, and particularity of different solar concentrator systems. Among these concentration technologies, reported in Table 1, only the solar tower and Beam-Down are suited for an integrated solar boiler with a pool boiling configuration. These two systems allow for high concentration factors (>1000) and working at high temperatures. At smaller scales, Beam-Down is preferred due to the lower construction costs and the convenience of receiving the concentrated solar power at the ground level.

Knowing the optical efficiency of the collection and concentration systems down to the receiver ( $\eta$ ), the DNI in W.m<sup>-2</sup>, the concentration ratio C (C = S<sub>mirror</sub>/S), and the solar field (S<sub>mirror</sub>), the concentrated solar power at the receiver can be determined:

$$\dot{Q}_{rad} = \eta. S_{mirror}. DNI . \tag{6}$$



Fig. 2. Presentation of conventional concentrated solar thermal system (example of solar tower)

Table 1. Characteristics and efficiency of different concentrated solar t	hermal
technologies [13].	

Technology	Parabolic trough	Solar tower	Fresnel reflectors	Dish Stirling	Beam-down
Collector shape	Parabolic trough	Heliostats field	Linear lame	Parabolic	Heliostats field
Concentration ratio	70 - 80 350 - 550	> 1,000 450 - 600	60 60	> 1,300 550 - 750	> 1,000
temperature (°C) Optical efficiency	0.60 - 0.65	0.58 - 0.78	0.40 - 0.50	0.85	570 0.40
(4) Particularity	-	-	-	Use a Stirling engine No storage	Two reflections

#### **Performance criteria**

In the present work, two performance criteria were retained to study different boiling scenarios: (i) the thermal efficiency of the boiler ( $\eta_{boiler}$ ), and (ii) the equivalent carbon footprints (expressed in kg-CO<sub>2,eq</sub>) using the global warming potential impact category (climate change, GWP100a) of the IPCC 2013 in Ecoinvent (version 3.4) [14], for 1kWh of steam energy produced.

For a conventional boiler, the thermal efficiency is defined as the ratio between the boiling thermal energy  $(\dot{Q}_b)$  and the input thermal energy supplied  $(\dot{Q}_{in})$ :

$$\eta_{boiler} = \frac{\dot{Q}_b}{\dot{Q}_{in}}.$$
(7)

The input heat  $(\dot{Q}_{in})$  of a fuel boiler is the product of the fuel mass flow rate and its heating value. When concentrated solar thermal systems are used for energy supply, the input heat is equal to the concentrated solar power at the receiver  $(\dot{Q}_{rad})$  given by Equation 6, and the boiling thermal energy  $(\dot{Q}_b)$  which represents the effective heat transferred to the fluid in the boiler as formulated by Equation 2.

#### **RESULTS AND DISCUSSIONS**

#### Thermal efficiency of solar boiler and importance of design parameters

The model is applied to a small and medium scale receiver, respectively with a diameter of 0.1 m and 0.5 m. The same DNI of 800 W.m<sup>-2</sup> was set for all the cases studied. The solar field has been defined according to the required area of the reflecting mirrors ( $S_{mirror}$ ) and has been adjusted to correspond to a beam-down installation with a typical optical efficiency ( $\eta$ ) of 0.4 and a concentration ratio (C) of 1,000. In addition, the following properties have been fixed for the receiver: emissivity ( $\epsilon_s$ ) of 0.8 representing the order of magnitude of emissivity for several conductive metals; rugosity ( $R_p$ ) of 50 µm; view factor (F) of 1 suitable for a flat or convex receiver surface.

The following Table 2 summarizes the thermal performances and capacities of the solar boiler for different receiver scales under two different boiling regimes.

<sup>nirror</sup> n <sup>2</sup> )
7.9
7.9
96.3
96.3

 Table 2. Thermal performance of solar boiler for different scales of receiver and two different boiling regimes

Overall, as expected, the solar boiler under nucleate boiling is more thermally efficient than the film boiling (with thermal efficiency of 56% for film boiling versus that of 79% under film boiling for a small receiver with d = 10cm). In addition to that, the performance of the solar boiler is not directly influenced by the size of the receiver in nucleate under the boiling conditions. Referring to Table 2, the boiling power transferred to the liquid ( $\dot{Q}_b$ ) in the case of nucleate boiling with the largest receiver (d = 50cm) is about 50 kW which corresponds to 69 kg.h<sup>-1</sup> of a pure generated steam. In this case, a solar field of almost 200 m<sup>2</sup> is needed, which is relatively small and suitable for the order of magnitude of thermal power in Beam-down

technology, for instance, the "Masdar City Abu Dhabi 100 kW<sub>th</sub> Beam-Down" with a solar field of 280.5 m<sup>2</sup> (first reflectors) and a secondary reflector at an altitude of 16 m, and land use of approximately 1,075 m<sup>2</sup> [15].

In Table 2, the performance of the solar boiler under film boiling decreases by increasing the size of the receiver. This can be explained by the increase in radiosity losses at the relatively higher temperature (1195.5 K) in the second case (50 cm receiver), compared to the first case (10 cm receiver) where the temperature of the receiver is 1135.4 K. However, it should be noted that the change in thermal efficiency under film boiling depends on both the heat transferred through the receiver and the surface of the receiver, therefore the surface of the receiver is not the only primary factor to consider. Depending on the required capacity of the boiler, the mirror area of the solar field is approximated, then depending on the technical constraints, such as the melting point of the receiver, the receiver area can be approached to improve the thermal efficiency, i.e. a lower surface temperature, and to avoid the melting.

Simulations were also carried out based on the 50 cm receiver with different view factors (F) in order to show the effect of the view factor on the performance of the boiler. The view factor can be changed by modifying the cavity effect of the receiver. The results are summarized in Table 3. As shown in Table 3, the view factor of the receiver has a large impact on the performance of the solar boiler; for example, decreasing F from 1 to 0.25 provides 18% efficiency improvement under nucleate boiling. It is important to note that a receiver with a view factor of around 0.25 is practically feasible to realize.

		-)
	Nucleate	Film
F	boiling	boiling
	$\eta_{\mathrm{boiler}}$	$\eta_{boiler}$
0.25	0.934	0.781
0.50	0.881	0.655
0.75	0.834	0.569
1.00	0.792	0.507

Table 3. Influence of view factor on the thermal performance of solar boiler (receiver diameter = 50 cm)

#### Comparing carbon footprints: industrial fuel boiler versus solar boiling

From the perspective of thermal efficiency, there is a considerable gap between a fuel combustion boiler and a solar boiler. Nevertheless, a stand-alone thermal comparison between the two approaches is not fair, as the fuel energy, in this case, is neither free nor renewable, while in the case of the solar boiler, the energy used is almost free and without involving the use of fossil fuels which implies both the depletion of resources and the emission of greenhouse gases. To take this point into account, a comparison of the carbon footprint was made between an industrial boiler operating on natural gas and a solar boiler.

Life Cycle Assessment was carried out on the two boiling scenarios, thanks to Umberto<sup>®</sup> software. The functional unit was the production of 1 kWh of steam power from boiling with a corresponding boiling capacity and over a lifetime of 20 years for the entire solar boiling process. The impact category of global warming potential (climate change, GWP100a) from IPCC 2013 in Ecoinvent (version 3.4) was chosen for the calculation of environmental impacts [14]. When considering the industrial boiler, the infrastructure, the electricity, and fuel consumption are taken into account, using the module *"heat production, natural gas, at boiler condensing modulation* <100 kW [Europe Without Switzerland] " of Ecoinvent dataset (Version 3.4).

Regarding the Solar Boiler, a receiver with a diameter of 0.5 is taken. The other parameters of the solar boiler are taken as follows: view factor 0.25, emissivity 0.8, DNI 800 W.m<sup>-2</sup>, Solar field 200 m<sup>2</sup>. The infrastructure of the solar field is taken into account. The construction of the boiler tank is considered equivalent to the construction of a gas boiler. For the supply of solar energy, the infrastructures are based on the dimensions provided in the literature [15]; these dimensions allow to estimate the quantity of steel, concrete, and mirror, as well as the number of motors required. The impact of the production of these materials was taken into account using the Ecoinvent dataset. The electricity necessary for the operation of the solar tracking and for pumping is taken into account using the low voltage market in Europe. The overall inventory of energies and materials used is given for 1 kWh of steam produced in Table 4.

Category	Material	Quantity	Unit	Process Ecoinvent
Equipment	Solar Boiler Tank	$4.07  imes 10^{-7}$	unit	gas boiler production [RER]
	Steel	$1.42  imes 10^{-2}$	kg	hot rolling, steel [RER]
	Mirror	$9.27 imes10^{-4}$	kg	flat glass production, coated [RER]
	Concrete	$1.44  imes 10^{-5}$	$m^3$	market for concrete, 20 Mpa [GLO]
	Motor	$4.88  imes 10^{-5}$	kg	electric motor production, for
				electric scooter [GLO]
Energy	Electricity	$1.86  imes 10^{-2}$	kWh	market group for electricity, low
				voltage [Europe without
				Switzerland]
	Solar energy	2.68	kWh	Energy, solar, converted [natural
				resource/in air]

Table 4. Inventory of materials for the calculation of the impact of 1kWh steam production with solar boiler

Based on the production of 1kWh of steam power, the equivalent carbon footprints for these two scenarios are: 0.297 kg.CO<sub>2</sub>-Eq in the case of a natural gas boiler and 0.016 kg.CO<sub>2</sub>-Eq in the case of a solar boiler with infrastructure included. It should also be noted that 67% of the footprints reported in the first case (natural gas boiler) are linked to the combustion of natural gas.

#### CONCLUSIONS

The present work aimed to study the performance of a solar boiler for the direct use of solar energy concentrated at the solar receiver. A simple and comprehensive model was developed and presented based on the main operating and design parameters of the solar boiler (shape, geometry, scale, and thermal properties of the receiver) under different boiling conditions (nucleate and film boiling) and the specificity of optical installations for the supply of concentrated solar energy.

Depending on the scale and boiling regime of the solar boiler, the thermal efficiency was between 0.72 and 0.86, which is smaller than that of an industrial fuel-fired boiler (0.95). However, comparing a fuel-fired boiler and a solar one from the perspective of thermal efficiency alone, is not fair, as fuel-based boiling requires fossil energy that is neither free nor renewable. The gain in equivalent carbon footprints in the case of a solar boiler, i.e. 0.281 kg.CO<sub>2</sub>-Eq avoided for 1 kWh of steam power produced when replacing a natural gas boiler with a solar boiler, makes it possible to fill the gap.

Although the thermal efficiency may decrease under the film boiling regime, the change in thermal efficiency under this boiling condition depended on both the amount of heat supplied to the receiver and the scale of the receiver, therefore in the case of film boiling, a combination of these two parameters (receiver scale and input power) should be investigated to achieve better thermal yields while meeting the physical constraints related to the material of the receiver for an operation at high surface temperatures. From a broader perspective, given the input of concentrated solar energy, the relevant study and optimization of such a solar boiler require taking into account all fundamental design parameters of the receiver, including the scale and choice of materials, geometry, and shape of its cavity.

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#### DESIGN OF AN EFFICIENT CHARGE CONTROLLER USED IN A SOLAR PV CHARGING STATION

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#### ABSTRACT

Solar photovoltaic (PV) systems are of great interest for electricity generation in recent days due to depletion of fossil-fuelled energy sources, global warming and clean environment. The use of these systems is mainly encountered in many applications that have been common in our daily life. These applications can be on-grid and off-grid power generation, charging stations for various electric vehicles (EVs) such as plug-in EVs, electric forklift, electric motor bike, golf carts etc. This investigation proposes an approach to design an efficient charge controller used in a solar PV charging station for charging EVs with various energy capacities. In such charging stations, maximum power point tracking (MPPT) plays major role in improving efficiency and there are few ways to do that, one is to employ a dc-dc converter based on switching mode devices. For the implementation of the charge controller, a DC-DC buck converter is considered to integrate a MPPT system in which the real coded genetic algorithms technique is employed rather than using deterministic iterative methods to rapidly and precisely find the maximum power point under varying environmental conditions. The designed system is simulated by MATLAB/Simulink and initial findings are consistent and promising, and will be given more in the full paper.

**Keywords:** Solar photovoltaic, global warming, fossil-fuelled energy sources, charging stations, maximum power point tracking.

#### **INTRODUCTION**

Nowadays, solar energy is being prevalent in renewable energy resource because of its feasibility and convenience. Solar energy becomes the surrogate origin due to depletion of conservative resource. Solar energy is effluence free, hygienic, and lavish in convenience and contains less overhaul. The coherence of photovoltaic system diminish gradually due to nonlinear features of PV array and atmospheric disorder. The maximum power at the output of PV array varies with respect to climate situation and illumination. [1] The way of converting sunbeams energy into electrically powered energy is done by PV scheme. A quantity of electrically linked solar chambers installed in a supporting assembly or mount is called PV units. [2] A solar PV system can be divided into two types, one is a Standalone PV system and the other is Grid Connected PV system. During the day, when solar energy is easily accessible, energy will store in battery that power can be used to feed the loads or the DC micro-grid in darkness or in cloudy weather. The solar control regulator used to charge the batteries in electric vehicles such as golf carts, forklifts, and electric motor bikes etc. [3] DC-DC converter topology use to distribute power among photovoltaic module and battery to be charged. DC-DC converter alters DC input voltage into DC output voltage, with size of smaller or greater than the input voltage. A lot of work has been done in the past years to design and build high-efficiency DC-DC converters that can be used in domestic solar systems. [4]

The main tenacity of this paper is to design an efficient regulator that will be used in solar PV charging systems. To withdraw the maximum power from the PV panel we use perturb and observe algorithm while adjusting the battery state of charge. [5] The DC-DC converter is used between the battery and solar array to reach maximum power. The buck charge controller

controls the battery via multi-stage charging approach in order to keep the battery in charging state effectively deprived of scarring it from excessive charging gas and overheating. The most frequently used type is the valve-regulated lead acid battery (VRLA) because it is inexpensive, maintenance-free, and highly efficient. [6] Although the cost of battery installation is relatively low compared to PV, the cost of battery life is significantly increased due to the limited service time.

#### PURPOSED METHODOLOGY

The purposed scheme established on four different parts: solar PV panel, solar regulator (MPPT), DC-DC converter, and battery. [7] Fig. 1 shows the general block diagram of solar charge regulator based PV system.

#### **PV PANEL**

In this system two series and ten parallel modules of PV array each of 190W power are being used. The open circuit voltage is 45.4V and the short circuit current is 5.44A. Two PV panels are connected in series so overall open circuit voltage is 90.8V. The description of PV array is given in table below.

Рмр	Cells V <sub>MP</sub>		IMP	β	α
190 W	72	36.2 V	5.25 A	-0.34401 %/°C	0.052996 %/°C

Table 1. PV Array Description

#### MPPT CHARGE REGULATOR

In solar panels, there is a peak spot wherever the voltage and current are on their peak value that specific point is called the maximum power point of solar panel. In a photovoltaic system, the current-voltage curve varies with respect to irradiance and temperature. When the environment is changed like most cloudy and sunny the temperature and irradiance also change. [8] By perturb and observe (P&O) method, MPPT based efficient regulator will design. The point where the voltage and current values are maxima known as the "knee" of the curve. Mainly used method of MPPT algorithms are: [9] Perturbation and Observation (P&O) algorithm and Incremental Conductance (IC) method.



Fig. 1. General Block Diagram of Solar based MPPT

#### PERTURB & OBSERVE (HILL CLIMBING) METHOD

In MPPT, hill climbing (P&O) method use to withdraw the extreme power from the system. In this method, due to a small increase in power change in the photovoltaic module. The output power is measured and compared with the old power and check if the system is reached to maximum point otherwise it increases the power until the maximum point is achieved. This is a commonly used method due to the ease of its implementation. In this method, perturbation is given to the PV array. If the PV module voltage is increased or decreased we can see the power is increased or decreased. [10]

In Fig. 2, the process of MPPT based (P&O) method is presented. The MPPT duty controller is being connected with the PV array and battery. It measures PV array and battery voltages. MPPT controller check battery voltages and see if the battery is fully charged or not. If charging of the battery is being reached its maximum point then the charge controller stops the charging to prevent battery overcharging. If the battery is not fully charged then the regulator charges the battery by using DC-DC converter. By measuring the voltage and current charge controller measures the new power and compares it with the old power. If the new power is bigger than the old power, to draw out the extreme power from PV plate we increase PWM based duty cycle. [11] If new power is smaller than the old power then we decrease the duty cycle so we can achieve our maximum point. Perturb and observe method is very simple to use and available at low cost with high precision.



Fig. 2. Flowchart of P&O Method

#### **DC-DC BUCK CONVERTER**

A step-down converter or dc-dc buck regulator converts the dc input voltage to regulated dc output voltage whose value is less than the input. The converter has a dc bias current and single voltage that allows controlling the voltage at output side is less than the input voltage level. By controlling the switching cycle we can maintain the dc stable output voltage. [12] The dc output is having some squared wave characteristics.

Buck converter operation divide into two modes, initially, the regulator is in open condition. When regulator is locked (closed) for first time the diode acts as an open circuit and the current starts to increase across the inductor after sometime current starts to decrease and voltage also decreases so at that interval energy will be stored in shape of magnetic field with the support of inductor. Initially the regulator is undefended the power stowed in inductor release energy across RC circuit. [13]



Fig. 1. Buck Converter Circuit Diagram

The duty cycle of buck converter can be measured by the proportion between the output voltage and input voltage as mention in equation 1. [14]

$$D = \frac{V_o}{V_{in}}.$$
 (1)

For a good estimation the inductor value can be calculated by equation 2, where D is duty cycle,  $f_{sw}$  is switching frequency,  $\Delta I_L$  is the inductor ripple current which is ten to thirty percent of output current, and  $V_o$  is the voltage at output side.

$$L = \frac{V_{out}(1-D)}{f_{sw}\Delta I_L}.$$
 (2)

Also, the minimum value of output capacitor can be calculated by equation 3, where  $\Delta I_L$  is the inductor ripple current, and  $\Delta V_{out}$  is the capacitor ripple voltage which is one to five percent of output voltage. Buck converter description show in below table.

$$C_{out(min)} = \frac{\Delta I_L}{8f_{sw}\Delta V_{out}}.$$
(3)

Inductor (L)	Capacitor (C)	Resistance (R)	V_out	Frequency (fsw)
500mH	1F	0.001ohm	12.98V	10,000Hz

Table 2. Buck Converter Specification

#### BATTERIES

Rechargeable batteries are energy-storing devices that transforms the one type of energy into another form. Nowadays, societies are using additional storage batteries instead of disposable equivalents for the reason of cost and environmental changes. [15] Lead acid battery with capacity of 12V 255Ah used in this system. The description of lead acid battery is:

Nominal	Rated	Initial	Maximum	Fully Charged	Discharge	Response
Voltage	Capacity	SOC (%)	Capacity	Voltage	Current	Time
12V	255Ah	0	265.62Ah	13.06V	51A	1s

Table 3. Lead-Acid Battery Description

#### **RESULTS AND ANALYSIS**

In Simulink model of standalone PV system, we see that PV panel is connected with MPPT and boost converter and then that boost converter link with buck converter to step down the input voltage to achieve our required voltage and that buck converter is connected with battery. Simulink Model of PV charging station is given in Fig. 4.



Fig. 2. PV Charging Station

To withdraw the maximum power at different irradiance from PV panel, MPPT (P&O) method will use. Boost converter connects with PV panel and PV panel is connecting to photovoltaic based (Perturb and observe) method. In Fig. 5 Simulink model of (P&O) method is displayed.



Fig. 3. Simulink Model of P&O Method

At STC (1000 W/m<sup>2</sup>), the output waveform of  $V_{PV}$ ,  $I_{PV}$ , and  $P_{PV}$  is shown in below figures, we also see that we reached our maximum value but there are ripple in voltage and current, we can reduce these ripple by changing the value of capacitor and inductor.







In this paper, buck converter uses to lower the boost converter voltage, to accomplish our desire output so we can charge the battery. We design a controller that can provide a PWM signal to the DC-DC buck converter. In this controller, first we compare our output voltage with reference voltage by using a comparator. The comparator output is a fault signal which is improved by using a gain amplifier. The output is assimilated but the integrator retunes by using timepiece pulse, the clock pulse frequency will be the sawtooth carrier wave frequency. Another comparator compares the saw tooth upsurge with the locus voltage and in response PWM signal is generated. Relay digitized the message i.e. in binary version zero (0) or one (1). Controller is given in fig. 9



Fig. 7. Buck Converter Controller

In below results, we see that when we run the circuit our voltage and current start increasing and our SOC of battery is at 0.01%. At time 0.7 sec our circuit reaches the require value like  $V_{out}=12.98V$  and  $I_{out}=50A$  and after that it takes time to stable the voltage and current. At 1.8 sec our required voltage and current is steady (constant) after 2.23 sec the battery starts charging and the value of SOC start increasing.



Fig. 8. Battery (Lead Acid) Charging (I)

Fig. 9. Battery (Lead Acid) Charging (V)



Fig. 10. Battery (Lead Acid) SOC (%)

Lead acid battery state of charge relates with lithium-ion battery state of charge in Fig. 11. We perceive that lithium battery charge fast as liken to lead acid but as relate to cost lithium batteries are affluent. So, that's why we use lead acid battery in our system.





Lead acid battery relates to nickel-cadmium battery and we proverb that nickel cadmium battery takes extra time to charge as liken to lead acid battery. The performance and settling time of lead acid battery is better than nickel cadmium battery.



Fig. 12. Lead Acid SOC relates to Nickel-Cadmium SOC
Batteries Intricacy		Distinguished Parameters	Settle down Time	Converges Speed
Lead Acid	Low	Voltage & Current	2.23s	Moderate
Lithium Ion	Moderate	Voltage & Current	2.18s	Fast
Nickel Cadmium Moderate		Voltage & Current	2.5s	Moderate

 Table 4. Comparison of Different Batteries

# CONCLUSION

In this paper, our main goal is to design an efficient charge controller that can charge our battery. From PV panel, maximum power will extract by using Perturb and Observe MPPT method. We design an efficient controller that can help our circuit in charging. The suggested method is capable of charging the battery at different Irradiation. Initially when we run the simulation, we observe that our voltage and current increasing linearly but at certain time it stops increasing because our battery needs 50A for charging. By results, we verify that the efficient controller charges the battery at constant current and at constant voltage. The design system is simulated in MATLAB/Simulink R2015a. This system will be used in home-based PV system, golf carts and electric bike.

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# TECHNO-ECONOMIC PERFORMANCE STUDY OF STAND-ALONE HYBRID SYSTEM IN LITHUANIA

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#### ABSTRACT

Becoming the world's first climate-neutral continent by 2050 is the greatest challenge and opportunity of our times. To achieve this, the European Commission presented the European Green Deal, the most ambitious package of measures that should enable European citizens, businesses and science to benefit from sustainable green transition. To make this transition large amount of wind and solar power will inevitably be used in EU countries. This paper analyses the technical and economical possibility of stand-alone hybrid power system for a small residential area encompassing 12 blocks of flats with 216 flats located in the suburbs of Klaipėda, in Lithuania. HOMER Pro software is used for energy system modelling. Main types of electricity generation and storage systems are overviewed, optimal system configuration options, dependence on environmental conditions are investigated.

**Keywords:** techno-economic, off-grid hybrid system, wind power, solar power, battery technology, Lithuania.

# **INTRODUCTION**

Climate change, rising fossil fuel prices and requirement all over the world for energy security have accelerated the progress of renewable energy sources. The traditional fossil fueldependent energy sector has significant human activity impact on climate changes [1]. To reduce the effects of human activities on the environment European Commission presented the European Green Deal. The European Green Deal is a new growth strategy to make the European Union's (EU's) economy sustainable. This will be achieved by turning climate and environmental challenges into opportunities and ensuring that the transition is fair and inclusive for all. The main objectives of the new strategy are as follows - there are no net emissions of greenhouse gases by 2050, the economic growth is decoupled from the use of resources, no person and no place are left behind [2].

Even though grid electrification is the first-choice of electricity supply in most countries, it is often un economical and expensive especially in low demand and isolated areas. A possible solution to this is to combine different renewable energy sources to form a hybrid system where a deficiency in the output of one system will be compensated by the other. These systems cost less, provide cheap power to remote villages, have shorter development period, are almost pollution free, are user and socially friendly and are important sources of energy for schools, hospitals and clinics, shops and public places in remote areas [3].

The HOMER Pro (Hybrid Optimization Model for Electric Renewables) software is appropriate for carrying out techno-economic, suitability, optimization and sensitivity analyses of hybrid renewable energy systems [4]. Therefore, a techno-economic and environmental performance assessment of a hybrid system is performed, using HOMER Pro software, a small residential area in the suburbs of Klaipėda, in Lithuania. The optimal configuration, relevant economics, electricity output of the hybrid system are being analysed in this study.

A remote prosumer (Fig. 1) consumes electricity at one point and produces it at a power plant in another location. These two points can also be adjacent plots or be in different parts of the country. All electricity supplied to the grid by a remote prosumer and recovered elsewhere

is charged for the use of the grid. In all other cases, it is subject to the same accounting principles as the average producer [5].



Fig. 1. A remote prosumer.

# METHODOLOGY

The Homer Pro 3.14.4 was used to design a hybrid renewable energy system that power generation is proposed for an off-grid remote household's village in the suburbs of Klaipėda, in Lithuania. Hybrid renewable energy system is a combination of different renewable energy sources such as photovoltaic (PV) cells, wind turbines, fuel cell etc. In this particular case, a system was designed considering that it could consist of solar PV panels, wind turbine and biodiesel-generator as power generators, Li-Ion battery for energy storage, and converter. Cost and lifecycle of separate components of the system are provided in Table 1. The system was optimized using a controller under the Loading Following (LF) strategy which is the optimal strategy for systems with a lot of renewable power that sometimes exceeds the load. The discount rate was used 5 % in calculations.

Component	Capital cost (\$/kW)	Replacement cost (\$/kW)	O&M cost (\$/kW/year)	Lifecycle (years)
PV system	600	400	10	25
Wind turbine	800	600	16	20
Battery	550	400	10	15
Biodiesel- generator	500	500	0.03 (€/op. hour)	15000 (hours)
Converter	300	300	0	15

Table 1. Capital cost, replacement cost, operational & maintenance (O&M) cost andlifetime of each component.

In addition, a summary of the available resources of the designed system (Fig. 2) including their characteristics can be seen below:

- PV system: a generic flat plate PV optimized by Homer optimizer was used for this analysis. Capital price for PV system was chosen like a large sun energy park price per kW.
- Wind turbine: a generic wind turbine with hub height 120 m was chosen for this analysis. Capital price for wind turbine was chosen like a large wind park price per kW.
- Biodiesel-generator: an auto-sized diesel generator with fuel consumption 0,236 l/hr/kW and fuel price 1 \$/l was used to ensure energy demand.
- Battery: the energy stored in batteries is used when there is insufficiency of solar and wind energy to meet the electrical energy demand. A generic Li-Ion battery was optimized by Homer optimizer and used in this study.



Fig. 2. Configuration of a hybrid renewable energy system.

### **RESULTS AND DISCUSION**

The hybrid renewable system was optimized by varying the capacity of wind turbine, PV cells, the number of batteries and the biodiesel-generator power output. The optimization results for Klaipėda suburbs are listed in Table 2 with a yearly mean wind speed of 7.31 m/s, and a biodiesel price of 1.00 /l. As demonstrated in Table 2, the optimal off-grid hybrid energy system is the wind / PV / battery which contains 187 kW PV panels, 390 kW wind turbine, 903 kWh Li-Ion batteries and 245 kW converter.

The cycle charging (CC) strategy is a dispatch strategy whereby whenever a generator needs to serve the primary load, it operates at full output power. Surplus electrical production goes toward the lower-priority objectives such as, in order of decreasing priority: serving the deferrable load, charging the storage bank, and serving the electrolyzer.

The load following strategy is a dispatch strategy whereby whenever a generator operates, it produces only enough power to meet the primary load. Lower-priority objectives such as charging the storage bank or serving the deferrable load are left to the renewable power sources. The generator can still ramp up and sell power to the grid if it is economically advantageous [4].

Table 2. Comparison of optimal hybrid system.

	Architecture										Cost		
m		<b>*</b>		2	PV (kW) ▼	G1 🍸	Gen (kW) ▼	1kWh LI 🍸	Converter (kW)	Dispatch 🍸	NPC (\$)	COE (\$)	Operating cost (\$/yr)
м.				2	187	390		903	245	CC	\$1.45M	\$0.130	\$32,498
				2		520		945	321	СС	\$1.53M	\$0.137	\$35,113
Ŵ		Ê		2	127	385	510	705	250	LF	\$1.84M	\$0.159	\$52,439
		Ê		2		440	510	760	243	LF	\$1.90M	\$0.165	\$57,227
		Ê				1,124	510			CC	\$4.01M	\$0.347	\$202,449
Ŵ		Ê		2	9.20	1,228	510		3.53	CC	\$4.03M	\$0.349	\$197,618
Ŵ		Ê		2	930		510	1,667	227	CC	\$4.13M	\$0.357	\$165,332
		Ê		2			510	497	361	CC	\$6.07M	\$0.525	\$385,502
Ŵ				2	5,449			4,043	485	CC	\$7.71M	\$0.695	\$147,159
м.		<b>f</b>		2	1,685		510		202	CC	\$9.05M	\$0.783	\$547,812
		Ê					510			CC	\$9.30M	\$0.805	\$641,867

This configuration corresponds to an initial capital of 994 131 \$, an operating cost of 32 498 \$/year, a total NPC of 1 452 152 \$, and a levelized COE of 0.13 \$/kWh under the CC dispatch strategy. Electricity price is 0.15 \$/kWh in Lithuania grid. So, this hybrid renewable system is competitive with grid.

The wind / battery hybrid power system is the second most cost-effective combination. Its total NPC is by 0.08 million \$ larger than the previous one. Moreover, its levelized COE is 0.137 \$/kWh. Furthermore, the NPC of wind / battery (1.53M \$) is lower than the NPC of PV / battery (7.71M \$) disclosing that wind / battery combination is significantly cheaper in comparison to PV / battery combination which leads to the leveled COE of 0.137 \$/kWh and 0.695 \$/kWh, respectively. The existing practice in Lithuania is that we use only PV parks for remote power parks and do not use wind turbines. Why?

In Table 3 the summary of calculated electrical data of the optimal hybrid system is provided.

Value	Electricity	Proportion,
	$(\mathbf{K}\mathbf{W}\mathbf{H}/\mathbf{Y}\mathbf{I})$	(%)
Production PV	208 021	10.8
Production wind	1 716 256	89.2
Production total	1 924 277	100
Consumption	794 540	100
Excess electricity	1 098 239	57.1

Table 3. Summary of calculated electrical data of the optimal hybrid system.

As listed in Table 3, excess of electricity is very high (57.1 % from production volume), much higher consumption. There is so, because power generation is cheaper according to huge energy storage. The system would be much more effective if we had cheap energy storage source like grid.

### CONCLUSIONS

Expansion of standalone hybrid renewable energy systems to households, small villages or telecommunication network stations where connection to the grid could never be possible, has led to an increasing interest in them.

The results obtained from technical and cost analysis showed that the combination of 187 kW PV module, 390 kW wind turbine, 903 kWh amount of batteries and 245 kW converter with the initial capital of 994131 \$, operating cost of 32498 \$/year and levelled COE of 0.13 \$/kWh could fulfil electrical load demand throughout the year and be competitive with ongrid energy price 0.15 \$/kWh.

The wind / battery hybrid power system is the second most cost-effective combination. The wind / battery hybrid power system is the second most cost-effective combination. Its total NPC is by 0.08 million \$ larger than the previous one, its levelized COE is 0.137 \$/kWh. It could be competitive with on-grid energy price too.

In future papers it could be analysed possibility of wind / grid system like a remote prosumer. To find and solve technological problems, offer the best ways to legitimize and develop the service.

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# EXTRACTION OF HIGH CALORIFIC FRACTION FROM MUNICIPAL SOLID WASTE DURING MECHANICAL BIOLOGICAL TREATMENT PROCESS

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#### ABSTRACT

Refuse-derived fuel (RDF) is a damp "fuel" typically obtained from Municipal Solid Waste (MSW) or commercial and industrial waste with analogous properties like MSW. It is typically pre-sorted and partially shredded residual waste with removed recyclable fractions. RDF characterize by high calorific value, which includes waste groups: plastics, paper, textiles, wood, and other. RDF is characterized by high variability in its morphological and quantitative composition reasonable.

RDF is produced from non-recyclable parts of the waste, which can be used in energy recovery processes. Production of RDF can minimize landfilling, reduce the potential of methane emissions to the atmosphere, and will allow the use of fertile land for their intended purpose. Energy recovery from waste can be enhanced through the initial estimate of the waste stream to increase its calorific value. The process separation of MSW at the Mechanical Biological treatment (MBT) plant and RDF production consists of several stages. The MSW after shredded, separated into different fractions by various processes: screening, magnetic separation, eddy current separation, optical separation (can be some stages), air classification. After separation at MBT plant, the calorific value of the RDF will decrease as high-calorific-value materials (plastics, paper, cardboard, textiles) will be sent for recycling. The EU currently has waste management regulations that allow the use of raw materials for recycling. So, there is the problem of how to add value to low calorific waste in RDF. One of the options for increasing the calorific value is heat treatment. Improving the energy of the resulting thermal treatment RDF will increase its attractiveness as an available fuel recovered from waste. This stage fits well into the "2025 Sustainability Goals" of "waste to carbon", "zero waste", and "circular economy" goals. The purposeful separation of MSW, physical and chemical treatment of RDF really can be exploited to maximize energy recovery by using no recyclable wastes.

**Keywords:** refuse-derived fuel (RDF), municipal solid waste (MSW), high calorific value, energy recovery processes, land filling, recycling

#### INTRODUCTION

Currently, there is an acute problem of handling production and consumption wastes, in particular, municipal solid waste (MSW). Lithuania has made notable progress in the waste management system. Since 2014, the proportion of waste that is disposed of in landfills in Lithuania has halved and this amount consists of 33 %. The recycling and composting process has become the general treatment process and consists 48 %, slightly above the EU (46 %). This tendency is in most of the part bind to the increase in composting volume (24 %) and attaches Lithuania as one of the top advance in the EU (the EU is around 17 %). A significant decrease in landfilling has been achieved by increasing combustion with energy recovery capacity (the second least favourable option for waste treatment), the rate of which doubled and consist 18 % since 2014; it may still increase in the near future (for example Vilnius). Lithuania is well on its way to compliance with the 50 % recycling of waste.

In Lithuania was the establishment of a deposit-refund system for plastic, glass bottles and metal cans. This important factor promoted the increase in the recycling of the recyclable fraction. This system became quite successful, achieving its 2020 objective of 90 % collection already in 2017. There are concrete strategies and plans to further optimization the separate collection system. At the end of 2021, there is a plan to optimize the collection items network and continue procuring the collection of waste containers for individual households. Since 2015 the Ministry of Environment conducts a public survey which shows that the citizen's opinion on waste management system becomes more favourable every year.

The magnification in composting is associated with the opening of green waste composting courts, where people can bring wastes from their home gardens free of charge. The Ministry of Environment of the Republic of Lithuania is also reviewed the more suitable ways of treatment with food waste.

But, more efforts will be needed for Lithuania to comply with post-target 2020, in particular as regards collecting more waste through the separate collection and decreasing reliance on MBT and waste incineration plants for the treatment of the biodegradable part of the waste. Lithuania introduced a landfill tax in 2016. The tax level is EUR 21.72 per tons with a gradual increase to EUR 44.89 per tons in 2020. The low tax rate in combination with waste disposal at landfill fees is an obstacle to improving the economic viability of recycling, as landfilling considered the cheapest waste treatment. Payment for the waste management service has to consist of two components: fixed and variable. The rules defining and explicating the scheme's realization are pretty blurred, however, and each municipality possesses a lot of versatility in how to implement it. If we look from the practical point of view, the fixed part of the fee is often predominant, and the variable part not always linked with the amount of collected waste. It is important that Lithuania has clarity on the real needs and plans for waste burning [1].

### Separation of raw materials for fuel

Environmental issues for fuel and its production process are crucial. The most important stage is the separation to remove chemically harmful components. Stones, glass and other inert impurities cannot be processed and impede it, while metals, polyvinylchloride (PVC), chlorine-containing and a number of other substances adversely affect the environment during combustion. With insufficient filtering of the fuel composition, dioxin, phosgene, cyanides enter the atmosphere. Therefore, the production of RDF fuels is a complex engineering challenge. Different types of recyclables contain:

- Particleboard and MDF contain formaldehyde resins;
- oil paint on items may contain lead;
- when organics rot, toxic substances are released;

- When burning tires, more than a dozen carcinogens are released.

The process of separation of municipal waste consists of several stages: separation of metals, biological fraction, inert fraction and further separation into paper, textiles, light plastics and solid plastics. Waste separation is a very important process, the bulk of which is curtailing the amount of waste that sent to the landfill. Waste segregation is also an inalienable part of the recycling of separated waste: plastic, paper, metal. The Fig. 1 shows scheme of mechanical-biological waste treatment in Kaunas MBT, Lithuania.



Fig. 1. Scheme of mechanical-biological waste treatment in Kaunas MBT

Ground tires, as an independent type of fuel, are used in the manufacture of cement, metallurgy, and energy. Increased requirements for environmental safety require equipping processing equipment with high-quality cleaning systems. Cleaning tire material is a multistage process, including magnetic separators, drum and vibration screens, air classifiers, etc. Fig. 2 presents the average morphological composition of municipal waste in Lithuania.



Fig. 2. Composition of municipal waste in Lithuania

Global waste growth will outpace population growth by 2050, with most of the trash being generated in urban areas. Global annual waste generation will increase from  $2.01 \cdot 10^9$  tones in 2016 to  $3.5 \cdot 10^9$  tones in 2050. Over 90% of waste in lower-income countries is taken to landfills openly and are not processed, as these nations often are away appropriate disposal and treatment facilities. There are 60 municipalities in Lithuania and it is the main institutions organizing municipal solid waste management. Separate collection system for municipal solid waste in Lithuania particularly implemented. The owners of individual houses can obtain the next waste collection bins: for paper, plastic and metals, for glass and for mixed residual waste, also composting bin for biodegradable waste. For apartments a modern waste collection bins for paper, plastics + metals, glass and mixed residual waste are used. In Kaunas city a mixed residues and separate MSW fraction by company "Kauno švara" ("Kaunas cleanliness") are collected (Fig. 3). At the Fig 3 you can see percentage amount of separate waste fractions by "Kauno švara".



Fig. 3. Separate waste fractions by "Kauno švara"

Separated collected fractions are additionally sorted by the same company, and mixed residues with high content of food waste is treated in Kaunas mechanical biological treatment plant, about 220 000 t per year. From all of these waste 29% consist from secondary raw materials (Fig. 4).



Fig. 4. Characteristics of MSW fraction after separation

After mechanical pre-treatment obtained high calorific fraction (52%) in Kaunas Cogeneration power plant are incinerated; and about (1.73%) of recyclable metals are extracted (Fig. 5).



Fig. 5. Fraction of waste to the WePt

Biologically treated fractions are used for remediation of Kaunas regional landfill. By "Kauno švara" annual collected amount of separate waste fractions (plastic, paper, metal, glass) is about 730 000 t. Not recyclable raw materials are sent to the Kaunas Cogeneration power plant. mechanical-biological treatment plants are designed to further treat mixed collected or residual municipal solid waste. The main aim of separation is to extract further value from the waste and to recover the energy contained in it while facilitating recycling and diversion of waste from landfills.

In the literature there were found six potential utilization for RDF. The existence some of these is rely on elimination any technical barriers for use of the fuel, the market sales, commercial drivers around carbon trading and energy costs, renewable energy incentives and the cost of waste disposal [2].

The six potential outlets are:

1. Industrial intensive users for power, heat or both.

2. Cement kilns.

3. Purpose built incinerators with power or power and heat.

4. Co-firing with coal at power stations.

5. Co-firing with fuels like poultry litter and biomass which are eligible for Renewable Obligation Certificates in conventional technologies

6. Advanced thermal technologies, such as pyrolysis and gasification which are Renewable Obligation Certificates.

The burning of RDF fuel, as well as the burning of unsorted MSW, entails the risk of the formation of highly toxic compounds of dioxins and furans. Therefore, this type of fuel is advisable to use in cement kilns, where high environmental effects will be achieved. This is due to the following:

- high combustion temperature of the material (T =  $1450 \text{ }^{\circ}\text{C}$  and more) and gas environment (T =  $2000 \text{ }^{\circ}\text{C}$  and more);

- alkaline medium of the material in the furnace in the presence of acid gases;

- significant gas residence time in the hot zone - more than 7 s at a temperature above 1200 °C, which ensures the decomposition of dioxins and furans;

- the movement of material and gases in counter-current;

- intense contact between solid and gaseous phases;

- the binding of even heavy and toxic materials in the presence of a liquid clinker phase;

- the presence of effective dust collectors in kiln plants.

In terms of economics and resource saving, 1.7 kg of RDF replaces 1 m<sup>3</sup> of natural gas.

## **Processing Municipal Solid Waste to RDF**

The process line for RDF production consists of several sequential devices that will carry out shredding operations to the required size. To date, waste from a composition that depends on the season and the behaviour of the population [5] is sent to the incineration to obtain energy. In the shortest time it will be real to choose the composition of waste that will have the greatest calorific value. Thus, there are challenges and opportunities to increase the value of low calorific waste by increasing its fuel properties, mass and volume through thermal processes such as torrefection. Reducing the volume, increase in calorific value RDF will increase its appeal as a fuel extracted from the waste [8]. This concept fits well into the goals of "carbon waste", "zero waste" and "circular economy". Torrefaction is based on the physical and chemical treatment of materials in the range of temperature 200 to 300 °C, chiefly at atmospheric pressure and without oxygen. The holding time (the also known as process for typical biomass) is between 15 and 60 minutes. At the Fig. 6 we can see RRF before and after torrefaction.



before torrefaction

after torrefaction

after mixing

Fig. 6 RRF before and after torrefaction

At the picture there are RDF after toreffaction by the temperature 200  $^{\circ}$ C during 20 minutes. In the issue of the thermal treatment of the RDF, the bulk of the treated material can decrease by 60%.

# **Alternative Fuel Production Requirements**

For efficient and safe use, RDF fuel must have certain characteristics and properties [14].

1. High calorific value, which is the determining factor when any fuel is introduced. The calorific value of RDF must be from 13 to 23 MJ/kg. Otherwise, it is not appropriate to introduce it as a replacement for conventional fuel.

2. Economic feasibility of implementing RDF. It is necessary that the cost of the alternative fuel produced, taking into account its delivery to the consumer (200 km), does not exceed 70 % of the cost of the traditional fuel used by the consumer.

3. Chemical composition and ash content of fuels. These values will influence the environmental content of RDF use. The base characteristics of the RDF fuel are presented in Figure 7.

4. Size and shape of particles. The size of the particles in different literature ranges from 20 to 60 mm. It would be better if the particles were even, sliced and ground.

To achieve the RDF characteristics listed above, appropriate waste management is required, as shown in Fig. 5. These operations are mandatory in the production of RDF. Waste briquetting can also be used in the production of fuel in the form of briquettes.

The fundamental characteristics of the fuel are also changed: volatile matter, ash content and fix carbon. Braking practically removes moisture and the fraction of organic compounds from the material [9, 10]. Fig. 7 shows the diagrams from laboratory studies.



Fig. 7. Results of investigation main characteristics of SRF before and after torrefection

The finished waste fraction was shredded to the size  $30\times30$  mm. The finished waste fraction was divided into two parts. The first part of waste was studied by defining the main physical and chemical properties of the RDF. The second part of the waste was subjected to thermal treatment (torrefaction). Torrefaction was carried out at different temperatures. From the above graphs, it can be seen that as the temperature grows, the number of volatile compounds decreases, and the number of ashes increases. The value of the fixed carbon remains constant for torrefaction part RDF.

Target separation and physical/chemical treatment of RDF can be used to maximize energy recovery in RDF. RDF has a high variability in its morphological and quantitative composition [11]. Since RDF is a mixture of various organic materials such as plastics, paper, textiles [12], it is reasonable to assume that different compositions of MSW may be affected the general energy demand and raw materials [8].

The waste fraction passed through the steps shown in Fig. 8 before conducting the basic fuel characterization studies. These stages were: separation (at Kaunas MBT), shredding (in the laboratory), mixing, drying and torrefaction.



Fig. 8. The steps of processing solid fuel from to RDF

The next step in preparing the torrefaction RDF was to form granules. The resulting mass

was pressurized after heat treatment without oxygen. The pressure produced the granules shown in Fig. 9.



Fig. 9. Granules after torrefaction RDF

In this work some earlier was writing, that high calorific value of RDF must be at least 13–23 MJ/kg. It was interesting and useful to know the calorific value of RDF and torrefaction RDF. We carried out a theoretical calculation of the calorific values of the considered RDF. Knowing the calorific value of each material in the samples and the weight of this material, we have made an appropriate calculation of the calorific value. From the literature it is known that the calorific value of RDF is increased by 20–25% as a result of torrefaction. In view of this fact the results of calorific value of the fuel from the waste were obtained (Fig. 10).



Fig. 10. Calorific value of fuel

There are two approaches to the production of RDF: the main, when a technology is implemented that aims to produce fuel, and the residual, i.e. extraction of high-calorie components from the formed after separation of secondary raw materials from waste. The first, main approach does not involve the extraction of secondary raw materials, which are more expensive and require less processing costs than RDF fuel. The second, residual approach has a large number of operations, including several stages of separation. This type of waste management was reviewed.

From the foregoing, we can conclude that the separation of solid waste in the MBT process is an important element of the process of obtaining high-calorific fraction, to obtain alternative fuel RDF.

## CONCLUSIONS

To sum up, proposed a waste separation process to isolate the high-calorific fraction plays an important role in recycling to cooperatively satisfy global energy demand. The RDF (refusederived fuel) is a burnable fraction of municipal solid waste. In this work to show that after separation there are a lot of materials that can be used for recycling or for creation samples of fuel with high calorific value. The diversity of materials after separation is showed by the example of Kaunas, Lithuania. Some developing countries use RDF for co-incineration with gas or coal or for aim to create power (cogeneration power plant). The process a thermal treatment RDF fraction can further enhance fuel properties and valorise RDF. The need for alternative energy for use in industrial sectors, for roasting, is one of the key factors necessary for expanding RDF production. To solve this problem, a model was hypothetically proposed for optimizing energy requirements after the waste separation process.

The proposed separation and thermal treatment can be useful for making specific decisions to optimize RDF production based on energy demand, which depends on the highly changing seasonal flow types of MSW and RDF.

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# TECHNICAL AND ECONOMIC STUDY FOR POSSIBILITY OF ELECTRICITY GENERATING BY WIND TURBINES IN SOCOTRA ISLAND, YEMEN.

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#### ABSTRACT

Renewable energy is one of the best methods that should be used to solve the problem of energy lacks, especially for isolated and far locations from electric grid. In this article, we will conduct economic analytical study of the possibility of electricity generation by wind turbines for Socotra. Also, give a study of the capacity factor, amount of annual energy produced from three types of turbines with different powers, and for three different heights, by Weibull distribution analysis for wind speed, according to the information of wind variables and forecasts of wind speed for some years in this location (using the time series analysis method), and will study electricity price and number of turbines necessary to cover the region's electrical need, for developing an integrated plan to study the project of producing electricity from the wind farms. By applying this study, we found that Weibull parameters which represent by shape parameter took values between 1.53 to 1.97 scale parameter reaches from 9.88 to 13.77 m/s, and electricity cost value from 0.076 to 0.096 \$/kWh. In addition, the number of turbines needed to cover Island electricity needs was identified, and excess energy from those turbines was estimated.

Keywords: Wind turbines, Time series, Weibull distribution, Capacity Factor.

## **INTRODUCTION**

Recently, renewable energy sources have a great interest because of the great demand for energy, and absence of these sources from pollution, which negatively affected of environment during the last period due to the large use of fossil fuels, which was the cause of emissions of pollutants such as carbon dioxide, carbon oxide, and nitrogen oxide, which have a role to global warming and expansion of the ozone hole, acid rain, etc[1] [2]. Add to that the renewable energy sources are permanent, sustainable, inexhaustible and low-cost compared to other sources, which made it one of the preferred sources of energy production for present and future, especially wind energy, which in the past years has great interest for their use, As the global production rate reached 1270 TW in 2018 [3]. The great use of wind energy will enable many countries to rely on their resources to generate electricity instead of fossil fuels.

According to the conditions in Yemen during the past years, such as the lack of oil derivatives and very large increase in their prices, which affected electrical energy production, solution must be found and in the fastest time to solve the energy shortage crisis, especially in

islands that are isolated areas from public institutions for energy production, and fuel prices rise recently. The best solutions are to use the region's natural resources and use it to produce electricity, which as it has natural resources such as wind, solar energy and other sources that enable it to produce energy to cover region's need. In this paper, the possibilities of producing electricity by wind turbines in coming years for Socotra Island, one of Yemen largest islands and the most in the population [4], are analysed.

The types of turbines differ according to the demand, region's need, location topography, and other variables. As it has different powers and types to meet need for any region according to its conditions and topographic. In this article, the study will be applied to three types of turbines with different power which are (Suzlon1000, Nordex1500, Gamesa2000) and at different heights (65,80,100) m to obtain sufficient information about the best ways and means to produce energy from wind with different variables. These types of turbines with medium powers were chosen instead of turbines of large powers (5000 or more) due to the presence of different wind directions in the region, so when installing farms, it should be taken into account that there are more turbines that correspond to those directions.

# SITE DATA

Socotra Island is located on the southern coast of Arabian Peninsula, specifically in a location facing the city of Mukalla, located on the eastern side of Gulf of Aden, on the eastern side of Africa Horn, it is located on latitudes (12.18 - 12.24) North of the equator and longitudes (53.19-54.33) East of Greenwich. The island is about 300 km away from the Yemeni coast, and an estimated distance of 900 km from the city of Aden. Socotra is an archipelago consisting of a group of islands. Socotra is the largest right-wing and Arab island, with the length of the island about 125 km, its width approximately 42 km, and the coastline is approximately 300 km long, Hadibu is the capital of Socotra, and total population of Socotra Island is about (80,000 people) [5].



Fig. 1. Socotra in map

## METHODOLOGY

## **Time series forecasting**

Because of the lack of information about wind speeds in Yemen, especially after 2014, we have to study forecasting wind speeds starting from 2014, time series method is one of the simplest ways to find forecasts of wind speeds where these speeds can be calculated and averaged by the seasonal distribution [6], and application of the following [linear trend model] equation:

$$\mathbf{T} = a + bt. \tag{1}$$

$$b = \frac{n\Sigma T_t \cdot t - \Sigma T_t \Sigma t}{n\Sigma t^2 - (\Sigma t)^2},$$
(2)

$$a = \frac{\sum T_t}{n} - b \frac{\sum t}{n} T_t, \tag{3}$$

where t = time, n - value number of time series, Tt - observed value.

The wind speed forecast calculated by applying the following equation:

$$F_t = s_t \cdot T, \tag{4}$$

where  $s_t$  is seasonal averages taken according to the desired division, either daily, monthly, quarterly, or semi-annually

#### **Weibull Distribution**

One of the most important factors for studying wind speed is to know the speed distribution information during any time are Weibull and represented by the k (shape parameter) and c (scale parameter)(m/s), as it gives accurate statistical information for all wind speed variables including the probability distribution of wind speed and the cumulative distribution that is given by the following equations[1], [7],[8]

$$f(v) = \frac{k}{c} \left(\frac{v}{c}\right)^{k-1} \times exp\left[-\left(\frac{v}{c}\right)^k\right].$$
(5)

$$F(v) = 1 - exp\left[-\left(\frac{v}{c}\right)^k\right],\tag{6}$$

where v is the wind speed, k and c calculate by

$$k = \left(\frac{\sigma}{v_m}\right)^{-(1.086)}.$$
(7)

$$c = \left(\frac{v_m}{\Gamma(1+\frac{1}{k})}\right). \tag{8}$$

$$\sigma = \sqrt{\frac{1}{n-1} \sum_{i=1}^{n} (v_i - v_m)^2} , \qquad (9)$$

where  $v_m$  is mean wind speed calculated by equation,  $\sigma$  is standard deviation of speed variation.

## Extrapolation of wind speeds at different hub height

Wind velocities are studied at different heights to find out the changes in that speed and in order to match turbines heights, which have tens heights of meters. Therefore, wind speed changes can be known with height by applying Equation (10) [7],[1].

$$\nu = \nu_0 \left(\frac{h}{h_0}\right)^{\alpha},\tag{10}$$

where v is the wind speed at the required height h, v0 is wind speed at the original height h0, and, ' $\alpha$ ' is wind shear exponent which has a value of 0.14 [5].

## Wind power, wind energy and capacity factor

The study of turbine power is very important to know the number of turbines that we need to cover the region's need and also we can infer the amount of energy produced for any time and turbines power can be calculated by the Equation (11) [1].

$$P = \frac{1}{2}\rho \int_0^\infty v^3 f(v) \, dv, \tag{11}$$

where  $\rho$  is the standard air density, 1.225 kg/m<sup>3</sup>, v is the wind speed, m/s. In the current study, the power of the wind was calculated using Weibull function and observed data. When the Weibull function is chosen as distribution function f(v), the average wind power density is calculated as below

$$p_m = \frac{1}{2} \rho_v^{-3} \frac{\Gamma\left(1 + \frac{3}{k}\right)}{\left[\Gamma\left(1 + \frac{1}{k}\right)\right]^3},\tag{12}$$

and we can calculate power extracted by the following [9]

$$P = \frac{1}{2}\rho C_p A \nu^3, \tag{13}$$

where  $A = \pi R2$  the area swept by the rotor in m2, and (Cp) is the capacity factor representing the ratio between the actual energy yields (Pout) over a period to the maximum energy yield (Pi)[7]

$$c_p = \frac{p_{out}}{P_i}.$$
 (14)

The output generated energy by wind turbines in the time T using Weibull distribution function can be expressed as follows[10]

$$E = T \int_{V_0}^{V_1} P_{(V)} f(v) \, dv.$$
(15)

## **Economic study**

The cost of turbine's changes according to manufactured country, turbine capacity, and tower height. The turbine consists of several parts, as shown in Fig. 2. The first part is the turbine which contain generator, gearbox, high speed shaft, low speed shaft, and electrical control and covered by Nacelle and fixed in front of the rotator that contains the blades. The second part is Tower and Footing and has differed in length according to need. The third part is the Transformer [11].



Fig. 2 Turbine main parts

It shows the price of the turbines nominal power per MW and tower heights in meters and it is worth noting that these prices may vary according to the country of manufacture and the technological development in manufacturing the turbines as well as the quality variation of the components.

	То	wer height	m	Reference
Nominal power (MW)	<100	100- 120	>120	
<2	1218	1341		[13],[14]
2 - 3.5	1128.5	1285	1497.5	

Table 1. Cost of wind turbines with nominal power and tower height \$/kW

To measure electricity cost, must know all of the investment cost Cinv (which includes the turbine cost, civil, electricity consumption, and engineering), the cost of operation and maintenance Comr, which is approximately 20% of investment cost and the additional costs Cs, and in most cases, it equals 10% of turbines. The present value of costs (PVC) is determined using equation(18) [7],[14].

$$PVC = C_{inv} + C_{omr} \times \left(\frac{1+i}{r-i}\right) \times \left[1 - \left(\frac{1+i}{1+r}\right)^t\right] - C_s \times \left(\frac{1+i}{1+r}\right)^t, \quad (18)$$

where r = interest rate = 2 %, I = inflation rate = 1.5 %, t = lifetime of wind turbine. For calculating kWh cost we should apply equation (19)

$$(kWh\ cost) = \frac{PVC}{PE}.$$
(19)

where PE= energy production in rated lifetime (about 20 year).

## DATA

The information was collected from several sources to meet the need for research, it can say that the sources of wind speed have been obtained from the Meteorological Authority Yemen, wind speeds were measured at hight of 10 m, which was satisfied with giving information for the wind speed from the year 2006 to 2010. The rest of the information and its limits were obtained in 2014. The last period before the collapse of the Yemeni government In Sana'a, the capital of Yemen, from the Weather Meteorological website (Info climate [15]). This site is characterized by giving detailed information on the hourly weather, including wind speeds, Turbine information has been collected from the website (wind turbine models), where it is characterized by a time to give all information about the turbines, their features and how they work[16], Where we will study wind turbines at three different powers and three different heights.

## **RESULTS AND DISCUSSION**

#### Mean wind speed

Table (2) shows the mean wind speeds from 2006 to 2014 for each month in which it was observed that the mean wind speed for all years is 9.17 m/s at hight of 10 m. The largest value of wind speeds is in June, July, and August, which have mean wind speed 14, 17.22 and 15.91 m/s respectively, while the lowest speeds are in February, March, April, May, October and November, where have mean speeds are between 4.37 to 6.8 m/s and the average speed is in the months January, September, and December, where have mean speed of 8 37, 11.4, and 7.91 m/s, This is information obtained from Yemeni Meteorological Authority and Internet websites that have been compiled for each month and year.

## **Time series forecasting**

By applying the time series method, we find that the amount of (a) in equation (3) equals 9.9 and (b) in equation (2) equals -0.0073 and with change in time (t) in Equation (1) and (4) we find Table 3, where appears that the annual and monthly mean wind speed from 2015 to 2025 are approximate values of the real wind speed in Table (2), and the Fig. 3 shows the difference between the real and forecasting values by applying time series.

	Jan.	Feb.	Mar.	Apr.	May.	Jun.	Jul.	Aug.	Sep.	Oct.	Nov.	Dec.	$v_{m.}$
2006	9.10	6.79	5.50	4.58	7.10	13.17	16.20	15.12	10.80	6.48	6.69	8.18	9.14
2007	8.95	6.33	5.71	4.84	6.84	12.86	12.09	13.07	10.75	4.94	6.33	7.72	8.36
2008	7.36	8.64	5.71	4.84	8.02	12.45	15.12	14.51	10.29	5.76	6.58	8.80	9.00
2009	8.18	6.89	6.07	5.35	6.64	11.63	16.67	15.64	11.01	8.80	8.18	10.39	9.62
2010	9.77	6.48	5.56	4.48	6.53	18.21	22.79	21.09	11.57	4.94	6.22	6.74	10.36
2011	8.50	6.00	6.20	4.50	6.90	13.00	16.70	14.50	11.80	5.00	6.60	9.00	9.05
2012	7.50	7.20	4.86	3.10	4.70	14.40	17.00	17.60	11.00	4.00	6.00	6.00	8.61
2013	8.50	6.70	6.00	3.90	8.70	15.60	20.00	16.00	10.80	7.30	6.40	7.20	9.75
2014	7.46	6.12	5.10	3.70	4.35	14.60	18.38	15.62	11.34	3.60	5.90	7.13	8.90

Table 2. Mean wind speeds for the years from 2004 to 2014 (real)

	Jan.	Feb.	Mar.	Apr.	May.	Jun.	Jul.	Aug.	Sep.	Oct.	Nov.	Dec.	$v_m$
2015	7.29	6.74	5.00	4.27	6.54	14.06	16.68	15.22	10.86	4.88	6.51	7.86	8.83
2016	7.22	6.67	4.95	4.23	6.47	13.93	16.52	15.07	10.76	4.84	6.44	7.78	8.74
2017	7.15	6.61	4.91	4.19	6.41	13.79	16.36	14.92	10.65	4.79	6.38	7.70	8.66
2018	7.08	6.54	4.86	4.15	6.35	13.66	16.20	14.78	10.55	4.74	6.32	7.63	8.57
2019	7.01	6.48	4.81	4.11	6.29	13.52	16.04	14.63	10.44	4.69	6.25	7.55	8.49
2020	6.94	6.41	4.76	4.07	6.22	13.38	15.87	14.48	10.34	4.65	6.19	7.47	8.40
2021	6.87	6.35	4.71	4.02	6.16	13.25	15.71	14.33	10.23	4.60	6.13	7.40	8.31
2022	6.80	6.28	4.66	3.98	6.10	13.11	15.55	14.19	10.12	4.55	6.06	7.32	8.23
2023	6.73	6.22	4.62	3.94	6.03	12.98	15.39	14.04	10.02	4.50	6.00	7.25	8.14
2024	6.66	6.15	4.57	3.90	5.97	12.84	15.23	13.89	9.91	4.46	5.94	7.17	8.06
2025	6.59	6.09	4.52	3.86	5.91	12.70	15.07	13.75	9.81	4.41	5.88	7.09	7.97



Table 3. Mean wind speeds for the years from 2015 to 2025 (forecasts)

Fig. 3. forecasting wind speeds from 2006 to 2025 using time series method

## Weibull Distribution

Mean wind speed (2014) at different heights  $\{10,65,80,100\}$  m, and applying the Equations (7), (8), (9) get the values of Weibull parameters as in Table 4 and it is observed that value of k and c increases with height

height2014										
Height m v <sub>m</sub> m/s Weibull parameter										
10	8.9	k=	1.53							
		c=	9.88							
65	11.5	k=	1.90							
		c =	12.96							
80	11.83	k=	1.90							
		c =	13.33							
100	12.21	k=	1.97							
		c =	13.77							

Table 4. Weibull parameters in different



Fig. 4 Weibull Probability density function

Thus, the probabilistic distribution of winds in region can be deduced, Fig. 4 shows the change in the probability density at the original height of measure 10 m, where its maximum value reached 0.076 at speed of 5 m/s, while the maximum value of the probability density at the height (65 m) is0.065 at speeds 8 and 9 m/s, (80 m) is 0.062 at speeds 8, 9 and 10 m/s, and (100m) is 0.062 at speed 10 m/s. It is worth noting that there is a slight congruence in the probability values between the last three heights, and this shows that the distribution of winds is converging at the three mentioned heights. As for the cumulative distribution of wind speed in notes, there is a perfect match at the altitudes of 65, 80, and 100 m, a slight difference at the original values of the height of 10 m as shown in Fig. 5.



Fig. 5 Weibull cumulative function

## Wind power, wind energy, and capacity factor

It is necessary when studying any project for wind farms, to make a clear vision and sufficient information for different types of wind turbines of different powers. Fig. 6 shows the change in the power of the turbines with wind speed for each of models (Suzlon1000, Nordex1500,

Gamesa2000) where the Cut-off wind speed is equal to 25 m/s and Cut-in wind speed is 2, 3, and 4 m/s respectively.



Fig. 6. Power curves of selected wind turbines.

It is normal for the power, energy, and capacity factor of the turbine change with the height according to the change of wind speed. Table 5 shows the change in the power of a turbine for one year, as well as the capacity factor, where the capacity factor increased by about 2% at each height. Wind speed and capacity factor have a direct correlation with power and energy of turbine, of course, that does not apply in all cases and with all wind speeds, by example in the large speeds that reach 23, 24 and 25 m/s, the increase in height increases in their speed, so these values are not available of the production of electricity, as the turbine cuts the energy when the wind speed reaches more than 25 m/s, and the decrease is indicated when analysing the results monthly basis, where we notice in Fig. 7, wind speed approaching 25 m/s in Aug and Sep are decreased with height, while that factor rises with the increase in height in other months, which are characterized by values smaller than 23 m/s.



Fig. 7. Capacity factor and energy production from three different turbines and three different height

Table 5. change of energy production (MWh) and capacity factor percentage of three different turbines with height (m)

Height	Variables	(Suzlon)	(Nordex)	(Gamesa)
45	Energy	4701.7	6307.72	8332.34
05	Ср	68%	61%	60%
	Energy	4819.64	6506.35	8596.17
80	Ср	70%	63%	62%
100	Energy	4966.32	6637.45	8765.86
100	Ср	72%	64%	64%

## **Economic study**

By observing Table (1) and applying the equations (18) and (19), we will find that the lowest price for the energy unit value is that produced by the turbine (Suzlon), which has the values 0.079, 0.076, and 0.081 \$/kWh, respectively, at the 65, 80, and 100 m, while the largest Energy cost is for the turbine Gamesa, which amounted to 0.096, 0.092 and 0.089 \$/kWh. For the turbine (Nordex) average values are 0.088, 0.083, and 0,089 \$/kWh, as shown in the Fig. 8, It is noticeable that energy unit cost is decreasing with height (80) m due to the low price of the tower and the increased energy produced at this height, as noted by decrease in energy unit price with an increased height of the (Gamesa) turbines is because the energy production capacity of this type of turbine increases with the increase in height, so it is noted that when considering the price of the energy unit, the best height in terms of price drop is at a height of 80 meters and the cheapest turbine is (Suzlon), but the turbines (Gamesa) and(Nordex) has more energy production capacity, at an average or large price, as needed.



Fig. 8. Electricity cost of three different turbines with different hub height

## The number of turbines needed to cover the region's need

The energy consumed per Yemeni person is estimated at 250 kWh during the year [17], and by knowing the population, we notice that the amount of energy required to produce is estimated at 20 GWh. If we know the amount of annual energy produced for each turbine, then we can calculate the number of turbines needed to cover the region's need, which is 5 turbines (Suzlon-1000kW), 4 turbines (Nordex-1500kW), and 3 turbines (Gamesa-2000kW) It was noted that they do not differ in turbines number at different hights but the difference is only in the amount of excess energy (excess than electricity cover need of Island) that can be used for

the storage in order to use when needed and to take into account the increase in the population in the region. Table (6) shows the number of turbines and the amount of excess energy for each turbine and for each height.

		Suzlon	Nordex	Gamesa
	Turbines Number	5	4	3
SSS SSS	65m	3508.5	5230.88	4997.02
xce nei	80m	4098.2	6025.4	5788.51
ΞΞ	100m	4831.6	6549.8	6297.58

Table 6. Turbines number and the amount of excess energy for each turbine and each height

# CONCLUSIONS

Socotra island has a distinctive wind speed, where the average speed is 8.9 m/s, which enables the production of electrical energy in addition to several features and conclusions that we summarize in the following:

- 1. A study of wind speed for the years from 2006 to 2014 confirms the presence of an amount of wind speed with values ranging between 8.36 to 10.36 m/s and an average of 9.8 m/s which is an amount of speed that enables the production of electric energy with high efficiency.
- 2. Weibull parameters increase with increasing height, as shape parameter took values between 1.53 to 1.97 and scale parameter reaches from 9.88 to 13.77 m/s, and the probability of distribution decreases according to height, while the cumulative distribution is noticed an almost perfect match at all height.
- 3. When using turbines with different powers and heights, we notice an increase in the amount of energy produced with height, as well as an increase in this capacity factor when studying these variables annually.
- 4. When studying changes in the produced energy and capacity factor monthly in a more accurate and detailed way, we find that it is not a condition that these variables increase with increasing height. It has been observed through study of those values decrease with increasing height, because largest speed values which approach 25 m/s increase when increasing height, Thus, these speeds are outside the possible speeds of energy production, as the turbine cuts energy production at speeds above 25 m/s.
- 5. In the economic study of energy unit cost, at height 65,80, and 100 m, we found that it ranged from 0.076 to 0.081 \$/kWh for (Suzlon1000 kW) turbines and from 0.083 to 0.089 \$/kWh for (Nordex 1500 kW). As for the turbines of (Gamesa 2000 kW) ranged between 0.089 to 0.096 \$/kWh. As it was noted that the price decreased with the increase in height to 80 m for Suzlon and Nordex turbines, as a result of the increased energy produced at this for the height, as well as the price of towers with values below 100 m, while the price of energy unit decrease with the height of the turbine is Gamesa, because of the large of energy produced from this High-power turbine.
- 6. By knowing region population and the amount of electric energy consumed for the Yemeni individual, it was found that we only need 5 turbines of (Suzlon 1000 kW), 4 turbines of (Nordex 1500 kW) and 3 turbines of (Gamesa 2000 kW) at three studied heights, but the difference appears only in amount of excess energy.

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# ONLINE FAULT DETECTION OF WIND TURBINES BY GENERATOR CURRENT SIGNAL ANALYSIS

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#### ABSTRACT

This experimental work aims to contribute to the online and early detection of wind turbine faults by applying a succession of approaches to the processing of components representative of the signal of the generator current. Compared with other fault detection techniques, MCSA (motor current signal analysis) is very effective as a technique for detecting mechanical and electrical faults that can affect wind turbine systems, among these advantages, it can rule on the degradation of the type of wind turbine defect because some anomalies are masked at low frequency and the difficulty of detecting them at birth remains very difficult. Our goal is to integrate this fault detection technique into a predictive and intelligent maintenance policy associated with modern computer technologies. The results obtained are satisfactory and reliable, the application of the MCSA allowed us to monitor the system online and to detect in a predictive, precise and rapid way the faults, their nature and their severity, such as unbalance which is cited as one of the main causes of degradation of rolling elements, the brush faults causing electrical asymmetries and consequently overheating with serious consequences for the production of wind energy, so we can in advance plan and apply a maintenance strategy without disrupting operation and production.

Keywords: Wind energy, predictive maintenance, generator, fault detection, MCSA

### **INTRODUCTION**

The monitoring of wind systems composed of a generator in the environment of green energy production is a fundamental task in particular, for high caliber ones, where downtime is very critical, given their importance [1-3]. Following mechanical alterations (unbalance, misalignment, fin degradation, erosion or clogging of the blades, ...), these systems are often subject to a bearing defect which represents the majority of degradations and which affects other parts of the machine, if these faults are not detected and repaired in time, the effects could be serious and costly.

In the presence of these faults, there are significant variations in the frequencies of the supply current, accompanied by vibrations and intense noise at the level of the transmission system of the machine and in the ambient environment in which it operates.

To diagnose mechanical faults on rotating machines, vibration analysis is a powerful method [4]. Only, it has shown its limits when it comes to defects inducing variations in torque

or defects almost imperceptible just at birth. To extract precisely the information relating to these breakdowns, research has been particularly oriented towards the MCSA (Motors current signature analysis) [5].

This experimental work innovates by the introduction of a series of on-line signal processing approaches by FFT (fast Fourier transform) and the STFT (short-time Fourier transform) applied to the supply current of the generator of the wind turbine. The application of this methodology allows a reduction in the detection time and it is relatively less bulky since it is only a question of picking up the current signal of at least one supply phase. In addition, it has the privilege of recommending simple and inexpensive equipment [6-8].

The experimental validation on the detection and diagnosis of the mechanical fault was carried out on a 4.05 KW generator, the various signatures obtained before and after repair are satisfactory and allow better confirmation of the nature of the degradation undergone by the wind power system, the results obtained can help establish a perspective of an automated diagnostic approach, the predictive detection and reliable diagnosis of these mechanical anomalies is necessary to avoid unfortunate financial consequences.

#### THEORETICAL BACKGROUND

It has been shown [9, 10] that mechanical faults internal and / or external to the motor cause oscillations of the torque which the induction motor picks up. In the presence of an oscillating torque, the surface current distribution which is sinusoidal for an ideal machine will be modulated in phase  $i_{to}$  (t) for an arbitrary phase, where  $\phi_A$ , denotes the phase angle of the modulation:

$$i_{to}(t) = i_s(t) + i_s(t) = I_s \sin(\omega_s t) + I_r \sin(\omega_s t + m\cos(\omega_c t - \phi_A) - \phi_r)$$
(1)

MCSA is industry-recognized failure detection and monitoring technique for these advantages. This technique makes it possible by analysing the current to detect mechanical and electrical faults.

Our experimental research focuses on the case of misalignment faults and defect of cage, outer ring and inner race of the bearing, the following relations show the relation of the vibration of the bearing to the current spectrum of the stator [11-13]:

$$f_{misalignment fault} = 50 \mp n f_r \tag{2}$$

$$\begin{cases} f_{outer \ race} = f_s + \ 0.4 \ f_r \ Z \\ f_{inner \ race} = f_s + \ 0.6 \ f_r \ Z \\ f_{cage} = f_s + \ 0.4 \ f_r \end{cases}$$
(3)

where  $f_r$  is the rotation frequency,  $n = 1, 2, 3... f_s$  is the supply current frequency, Z expresses the number of balls.

The short-time Fourier transform offers a two-dimensional (time - frequency) signal, also known by sliding window FT (Fourier transform) is a development that extends the technique of standard FT to handle non-stationary data.

The idea is to analyse the signal window by window. The FT of each windowed signal portion is calculated as follows: [14].

$$STFT_x^w(\tau, f) = \int_t x(t) \cdot w^*(t-\tau) \cdot e^{-j2\pi f t} dt , \qquad (4)$$

where:

x(t): represents the sampled time signal.

 $w(t){:}\xspace$  the time window of width T and centered at which allows extracting a portion of signal.

w\* : denotes the conjugate complex of w.

# EXPERIMENTAL CONTEXT

For the realization of this test, we have voluntary degraded the coupling connecting the generator. The coupling that is supposed to tolerate misalignment. If a rigid mechanical coupling were used, damaging loads can be transferred from one shaft to the other and prematurely wear bearings and equipment on both sides. In our case of wind turbine, the coupling is used on the two speed shaft (750 RPM, 1400 RPM) of the gearbox to drive the generator.

The acquisition of the signals was carried out by means of a HAMEG507 oscilloscope with a sampling frequency between 1 kHz and 2.5 MHz connected to a current sensor.

Fig. 1 presents the experimental test bench made up of the entire online wind turbine detection system based on a generator: 4.05 kW; 50 Hz; 220/380 V; 13 / 7.5 A.  $I_a$ ,  $I_b$ ,  $I_c$ : phase currents.



Fig. 1. Test bench

Data processing is done using MATLAB software for FFT and STFT spectrum analysis which provides us information used for diagnosing possible anomalies such as load issues, rotor misalignments or bearing faults.

# **RESULTS AND DISCUSSIONS**

Fig. 2 shows the healthy case of the generator, Fig. 3 represents the FFT spectrum of the degrade case of the system at the speed 750 RPM, noticing the appearance of harmonics at multiples of the frequency of rotation of the rotor of the generator (12.7 Hz, 25.39 Hz, 37.11 Hz). These harmonics which appear at the multiple of the frequency of rotation inform us about the exact nature of the fault; in our case it is a coupling fault, this frequency appears around the fundamental at frequencies  $(2.f_r)$  which subsequently damages the bearings of the generator.



Fig. 3. FFT spectrum of the degraded generator

Among several advantages of frequency domain analysis for non-stationary signals, STFT is a reliable approach to analyse signals obtained under complex conditions. Fig. 4 shows the STFT spectrogram of the healthy generator.

To effectively apply STFT to media fault signals, the STFT matrix is determined with the MATLAB tool to achieve high precision and computational efficiency. After having analysed what segment duration of the signal has essential characteristics, Fig. 5 illustrates the spectrogram in the case of a cage defect, outer race and inner race fault of the bearing, when the generator is running at 1400 RPM to vary and double the speed in order to diagnose and study the behaviour of the generator current at variable speed.



Fig. 4. STFT spectrogram of the healthy wind turbine system



Fig. 5. STFT spectrogram case of a bearing fault

By comparing the experimental results obtained, we observe on the spectrogram a variation of the colours on the bands corresponding to the frequencies of the faults: 18.66 Hz, 96.66Hz, 149 Hz, and 223 Hz, the reading of which on the colour scale shows evolution of the noise density when passing from the healthy state to the degraded state.

# CONCLUSION

In this paper, an approach to on-line fault detection in a wind power system is presented, by analysing the current signal (MCSA).

The results obtained during this experimental work demonstrate that the exact nature of the type of degradation that affects the system has been detected, by analysing the signatures of healthy and degraded operation obtained by MCSA. Numerous research results have been obtained using this technique. in the diagnosis, electrical damage and mechanical damage (misalignment, bearings, etc.) undergone by the electrical drives.

This technique can be integrated into a predictive and intelligent maintenance platform that would be able to ensure the reliability of diagnosis and predictive detection of anomalies affecting the elements as well as maintenance management.

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# EFFECTS OF MPPT PARAMETERS ON THE PERFORMANCE OF PHOTOVOLTAIC INVERTERS

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## ABSTRACT

The increasing share of renewable energy-based power plants in electricity generation poses some requirements for power electronic converters. Power electronic converters can be expressed as an operational interface between the grid and photovoltaic modules. In this context, they operate as a key component in terms of increasing efficiency and providing the power quality standards defined in the grid codes. Maximum power point tracking techniques that are utilized as a controller part of the converters have crucial effects on both efficiency and power quality issues. For iterative maximum power point tracking techniques sampling frequency and perturbation step size are the major parameters that need to be optimized by considering the converter dynamics. The low sampling frequency causes instability due to the slow perturbation of the operation point, especially under fast-changing atmospheric conditions. On the other hand, the perturbation step size can also affect the performance of the converter in regards to both efficiency and harmonic levels. From the power quality point of view, these two parameters induce harmonics in the output current of the inverter. Moreover, the selected parameters that are not optimized, severely decrease the efficiency rate of the overall system. In this paper, impacts of maximum power point tracking technique parameters will be investigated for twostage grid-connected photovoltaic systems. An improved genetic algorithm-based maximum power point tracking technique is proposed to increase the efficiency level and reduce the harmonic rate in the output current by conducting simulation studies.

Keywords: Renewable Energy, MPPT, Photovoltaic, Inverter, Harmonics.

#### INTRODUCTION

The rapid growth of technological developments, industrialization, and population makes efficient utilization of electrical energy a primary concern. The generation of electrical energy highly depends on fossil fuels. However, economical and environmental issues due to the intensive use of fossil fuels encourage people to emerge alternative energy sources [1]. Among the alternative energy sources, solar energy is envisaged as a promising option for sustainable, eco-friendly, and low-cost electrical energy generation [2]. Photovoltaic (PV) systems, that are capable of converting solar energy to electrical energy attracts much interest in recent years [3]. These systems can be considered as three parts as shown in Fig. 1.



Fig. 1. Block diagram of a PV system

Power electronic converters can be highlighted as operational interfaces between the PV modules side and user side. Approximately more than 98% of installed cumulative PV power in Europe is directly injected to the grid [4]. In grid-connected PV systems, inverters operate as functional conditioners between the PV modules and the grid. Controllability of the inverters ensures power flow control, fulfilments of power quality demands, and high efficiency of the overall system. Maximum power point tracking (MPPT) techniques seem as crucial control algorithms for inverters [5]. It is possible to overcome the challenges such as adjusting power flow, increasing efficiency, and eliminating power quality issues. However, MPPT parameters should be well optimized to obtain robust and reliable operations. Hence, the operation of MPPT and the parameter selections primarily affect the overall performance of the system [6].

From the efficiency and power quality point of view, many studies have been carried out in the literature. In [7], the sampling interval parameter of the P&O MPPT technique is optimized according to the utilized converter dynamics. Due to causing instabilities, the sampling interval is adjusted by taking the atmospheric conditions into account. In [8], the parameters of the P&O must be adopted to the dynamic behaviour of the specific converter. The overall system efficiency is increased by decreasing the oscillations. In [9], it is indicated that the performance of the system depends on the amplitude and the frequency of the perturbations. An online perturbation period is proposed. In [10], a sliding mode control-based variable step size P&O MPPT technique is proposed to improve convergence speed. The particle swarm optimization method is utilized for sliding mode controller gains. In [11], to eliminate the drawbacks of the conventional P&O, a smart oscillation, an intelligent prediction method is presented to cope with the partial shading conditions. In [12], artificial neural network (ANN) and P&O-based hybrid MPPT technique is proposed to eliminate the slow convergence speed issue of the P&O MPPT technique. The ANN-based model generates reference for P&O under deep changes in atmospheric conditions to increase the convergence speed and decrease the number of oscillations.

In this paper, the effect of MPPT parameters on performance criteria such as power oscillations and output current total harmonic distortion (THD) are investigated. Also, overall system efficiency is evaluated by different MPPT parameters. The simulation results revealed that the dynamic response of the overall system is highly dependent on the MPPT parameters. The low sampling frequency primarily affects the accurate detection of the maximum operating point. On the other hand, small perturbation step size reduce the dynamic response of the system and induces instabilities. The instabilities of the system increase the distortion of the output current and also reduces the overall efficiency.

The rest of the paper is organized as follows. In Section 2, the modelling of the PV module is presented. In Section 3, system description is ensured. Simulation results and discussions are provided in Section 4. Finally, some conclusions are given in Section 5.

#### **PHOTOVOLTAIC MODULE**

A generalized single diode PV cell model with a series and parallel resistances is built in the PSCAD/EMTDC software environment with FORTRAN coding. The mathematical expression of the PV module that includes the series and parallel connection of cells can be shown as [13].

$$I_{pv} = I_{ph} - I_o \cdot \left( e^{\frac{V_{pv} + I_{pv} \cdot R_s}{AV_t}} - 1 \right) - \frac{V_{pv} + I_{pv} \cdot R_s}{R_{sh}}.$$
 (1)

The simulated model is also validated by comparing the characteristic curves under different irradiation values provided in the datasheet of the PV module and simulation results. It is observed that the characteristic curves are almost the same. The characteristic I/V curve of the simulated PV module is illustrated in Fig. 2.



Fig. 2. The characteristic I/V and P/V curves of the simulated PV module

#### SYSTEM DESCRIPTION

A two-stage grid-connected PV system is modelled to analyse the effects of MPPT parameters on both efficiency and power quality issues. The power circuit topology consists of a PV array, boost converter, full-bridge inverter, output filter, and grid. The control block includes MPPT and synchronous reference frame-based control block. The boost converter is utilized to increase the input voltage and ensure the operation of the PV module at the MPP. The boost converter design depends on the selection of the inductor, the input and output capacitors, the power switches, and the output diodes. It is worth pointing out that the accurate selection of the inductor and capacitor values mainly influences the ripples in the input and output waveforms. It should be noted that the ripples fundamentally disrupt the MPPT controller performance and reduce the overall efficiency of the system. On the other hand, these ripples have an impact on the lifespan of the converter components especially capacitors. The limit values of the ripples on the current and voltage are defined as 10% and 1%, respectively. The switching frequency of the DC-DC converter is specified as 20 kHz [14, 15]. The design equations are given below.

$$L_{boost} \ge \frac{V_{out}(1-D)D}{f_s \Delta I} \,. \tag{2}$$

$$C_{in} = \frac{I_{out-max}D^2}{0.02(1-D)f_s V_{in}}.$$
(3)

The boost converter is designed to operate in continuous conduction mode. The state-space equation of modelled boost converter is provided in Eq. 4.

$$\begin{bmatrix} \dot{i}_L \\ \dot{\hat{v}_c} \end{bmatrix} = \begin{bmatrix} 0 & -(1-D)/L \\ (1-D)/C & -1/RC \end{bmatrix} \begin{bmatrix} \hat{i}_L \\ \hat{\hat{v}_c} \end{bmatrix} + \begin{bmatrix} 1/L & 0 & V_0/L \\ 0 & -1/C & -I_L/C \end{bmatrix} \begin{bmatrix} \hat{\hat{v}_g} \\ \hat{\hat{i}_z} \\ \hat{d} \end{bmatrix}.$$
 (4)

Also utilizing the state-space averaging model, the small-signal transfer function of the boost converter is derived as below.

$$\frac{\widehat{V_o}}{\widehat{d}} = \frac{7.84x10^5}{s^2 + 92.3s + 3.92x10^5}.$$
(5)

The bode plot of the utilized converter is illustrated in Fig. 3.



Fig. 3. Bode plot of the utilized converter

The perturb and observe (P&O) MPPT technique is used for extracting maximum power from the PV panels by controlling the DC/DC converter. In addition, a method that utilizes the symbolic regression analysis to find the best suitable mathematical function is employed. In this context, the MPPT parameters sampling frequency and perturbation step size are varied to observe the impacts on both efficiency and power quality issues.

The power extracted from the PV modules is injected to the utility grid through a fullbridge inverter with an LCL filter. The injected power is controlled by synchronous reference frame-based control block. The resonant frequency of the filter specified to be nearly 3.5 kHz. Ripple tolerance of the filter is taken as 10%. The filter parameters are given in Table 1.

Table 1. LCL filter parameters

Li	Lg	Cf	Rd
3.7 mH	0.75 mH	3.2 uF	4.5 ohm

The bode plot of the designed filter with the calculated parameters is provided in Fig. 4.



Fig. 4. The bode plot of the designed filter

## SIMULATION RESULTS AND DISCUSSIONS

A two-stage grid-connected PV system is simulated by utilizing the PSCAD/EMTDC software to perform the analyses of MPPT parameters over the entire system. The modelled PV modules are connected in series to constitute a 1 kW installed power. The input voltage range of the boost converter is determined to be between 160 V and 200 V. The maximum power is extracted from the PV modules and the input voltage is increased to 380 V through the boost converter. Then, the extracted power is injected to the utility-grid by a full-bridge inverter.

P&O MPPT technique is used to analyse the effects of sampling time and perturbation step size over the performance of the entire system. To perform detailed analyses several case studies are conducted. In the first case, the step size is adjusted to be 0.1 s and then changed to 0.05 s. The irradiation level is also changed from 1000 W/m<sup>2</sup> to 600 W/m<sup>2</sup>. The main objective is to demonstrate both steady-state and transient responses with different perturbation step sizes. The obtained results are shown in Fig. 5.



Fig. 5. The obtained results for different perturbation step sizes

The results indicate that small step sizes dramatically reduce the dynamic response of the overall system. The convergence speed decreases while the rate of overshoot in output power is getting higher. In addition, output current THD also rises for small perturbation sizes, especially under low irradiation levels. On the other hand, output power oscillation is substantially reduced thanks to the small perturbation step size. The efficiency of the overall system is negatively affected by the small perturbation step size.

In the second case, the sampling time is adjusted to be 0.01 s and then changed to 0.1 s which corresponds to the sampling frequency of 100 Hz and 10 Hz respectively. The irradiation level is also changed from 1000 W/m<sup>2</sup> to 600 W/m<sup>2</sup>. The main objective is to demonstrate both steady-state and transient responses with different MPPT sampling frequencies. The obtained results are given in Figure 6.



Fig. 6. The obtained results for different sampling times

The obtained results show that increasing sampling time interval considerably reduce the efficiency of the overall system due to the low convergence speed. The rate of overshoot in output power is increased while the output power oscillation is substantially reduced. In addition, the tracking accuracy is negatively affected. On the other hand, the output current THD is almost the same for different sampling time intervals.

To solve the aforementioned MPPT parameter-based efficiency and power quality issues an improved genetic algorithm-based MPPT technique is developed. The developed MPPT technique remarkably improves the dynamic response of the overall system. The instabilities that increase the output power oscillations and deterioration of output current are eliminated. Also, the output current THD is noticeably suppressed. The obtained results for irradiation level changed from 1000 W/m<sup>2</sup> to 600 W/m<sup>2</sup> are illustrated in Fig. 7.



Fig. 7. The obtained results for the developed MPPT technique

#### CONCLUSION

In this paper, the effects of the MPPT parameters named sampling frequency and perturbation step size on both efficiency and power quality issues are investigated. The rigorous model of the two-stage grid-connected inverter and its design stages are highlighted. The performance of the system is evaluated under steady-state and dynamic conditions with different sampling frequency and perturbation step size values of the P&O MPPT technique. Moreover, a mathematical model-based MPPT technique is proposed to enhance the performance and efficiency of the overall model. The obtained results indicate that perturbation step size highly affects the convergence speed which induces instability for the entire system. Thus, the output current THD increases for the small perturbation step size. In addition, the efficiency rate of the overall system decreases. On the other hand, the sampling frequency of the MPPT technique has impacts on the transient behaviour of the controller. Tracking accuracy and convergence speed have a direct relation to the sampling frequency.

An improved genetic algorithm-based MPPT technique improves the transient response of the overall system. The output current THD is substantially reduced to the value below 4% while the system's overall efficiency is increased by 2%.

#### ACKNOWLEDGEMENT

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# CONFERENCE PAPERS

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# BIOGAS PRODUCTION FROM CHICKEN MANURE AT DIFFERENT ORGANIC LOADING RATES

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#### EXTENDED ABSTRACT

#### **OVERVIEW**

As the world's energy demand is constantly rising, there is a need for sustainable energy production increase. In order to mitigate the effects of global warming, the world must significantly reduce greenhouse gas (GHG) emissions in every sector, in particular, from fossil sources. There are various methods available for the treatment of organic wastes and bio-based energy production but the anaerobic digestion (AD) appears to be one of the most promising approach [1] for producing environmental and socio-economic benefit, in terms of renewable energy (biogas), reduction of organic wastes going to landfills and abatement of GHG emissions [2]. Animal slurry and poultry manure are recognized to be a very favourable substrate for biogas production. It has been estimated that world produces around 20 708 million tons, Asia produces 11 514 million tons and Europe produces about 2039 million tons of chicken manure annually and 70–60% to this manure remains undigested. Therefore, it is expected that together with anaerobic technology development, research driven innovation and strong political push towards climate neutrality in the world, the chicken manure anaerobic digestion capacity will double in the nearest future.

The objective of this study was to evaluate chicken manure biogas potential and to explore the full-scale biogas plant digestion performance in order to better understand the stability of chicken manure digestion process. The major factor to overcome the ammonia inhibition was fresh water dilution strategy and the process adaptation strategy towards improved anaerobic digestion of chicken manure as a mono substrate in a full-scale anaerobic digestion plant.

#### **METHODS**

Chicken manure (CM) samples were measured before the biomethane potential tests (BMP) were performed. Digestates from full scale anaerobic digestion plant were measured immediately after sampling date. The measured chemical parameters were the dry mass (DM), volatile solids (VS), Total Kjeldahl Nitrogen (TKN), Phosphorus (P), Potassium (K), organic carbon (OC), pH and ammonium nitrogen (N–NH4) both for fresh chicken manure and chicken manure digestate. The BMP test temperature was mesophilic ( $35 \pm 1 \, ^{\circ}$ C) and the chosen test duration was set to 40 days. The working bioreactor volume was set to 0.4 L. The chosen inoculum to substrate ratio was 2 on g VS basis.

The continuous biogas production experiment was carried out in full scale anaerobic digestion plant located in Lithuania. The bioreactor with a working volume of 2500 m<sup>3</sup> was operated continuously at  $35 \pm 1$  °C with four mixers stirring once every hour for 15 min mixing interval. The duration of the experiment was 217 days.

#### RESULTS

The biogas production slope indicated that after 15 days of incubation more than 90% of chicken manure biogas potential was produced. The biomethane potential test of collected CM samples show the specific biogas production of  $145\pm57$  L biogas kg<sup>-1</sup> CM added. The lowest CM biogas yield was found to be 88 L biogas kg<sup>-1</sup> CM added.

Periods		1	2	3	4
Experiment period		Stable	Imbalance	Acclimatization	Acclimated
Experiment duration	days	25	21	60	111
Biogas production	m <sup>3</sup> t VS added	504	466	486	489
<b>Biogas composition</b>	% CH <sub>4</sub>	60	53.3	57.9	58.6
Hydraulic retention time	days	42	35	34	45
Organic loading rate	kg VS m <sup>-3</sup> d <sup>-1</sup>	2.22	2.24	2.27	3.14
VFA	gL <sup>-1</sup>	3.7	7.37 (peak at 10.8)	9.13	7.86
N-NH4	gL <sup>-1</sup>	3.94	4.09	5.09	5.41
рН		8.04	7.4	7.98	7.96
FAN	mgL <sup>-1</sup>	604	598	566	542
Temperature	°C	40.3	40.4	37.4	36.1
Process efficiency	%	95.08	78.15	88.64	90.02 (peak at 93%)

#### CONCLUSIONS

As the demand for renewable energy is growing, chicken manure becomes an attractive feedstock for biobased energy production. The BMP results indicate that chicken manure produces  $312\pm 23$  L CH<sub>4</sub> kg<sup>-1</sup> VS added and the biogas yield per quantity of wet mass depends on the volatile solids fraction in the manure biomass. The results obtained from the full-scale anaerobic digestion plant from the 217 days' operational period of chicken manure digestion as a mono substrate indicated that there is time required for acclimatization phase of the anaerobic digestion process. This acclimatization should be performed by continuous steady supply of chicken manure into the bioreactor while maintaining constant organic loading rate. The acclimatization phenomena can be related to ammonium concentration in the fermentation media causing partial inhibition, which is reflected in biogas volume as well as energy content reduction. However, the data analysis of anaerobic digestion performance indicates that the system is able to adapt and acclimate to increased nitrogen concentration in the media. Once adapted, the performance of biogas plant fermenter was able to deliver 93% of chicken manure biogas potential with a OLR of 3.14 kg VS L<sup>-1</sup>d<sup>-1</sup> and TAN concentration of 5.5 g L<sup>-1</sup>.

Keywords: Anaerobic digestion, biogas, chicken manure, ammonium inhibition, full scale digestion

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# POTENTIAL OF GHG EMISSION SAVINGS IN HOUSEHOLD SECTOR BY REPLACING TRADITIONAL SOLID BIOMASS BOILERS WITH NOVEL STIRLING ENGINE BASED MICROCOGENERATION SYSTEMS

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#### ABSTRACT

Households make up about a third of Latvia's final energy consumption, which accounts for the largest share of fine particulate emissions. Out of 817,900 households, 356,590 are not connected to district heating and heat supply is provided by local heat sources. Most households use wood stoves or boilers as individual heating equipment. The condition of those heating equipment is often assessed as very poor, most of them are powered by firewood and are at least 25 years old and its efficiency is lower than 60 %. Only a small part is high efficiency equipment. Statistic data shows that the primary heat consumption in the country, of which DH accounts for 26 % and individual heat supply 74 %, besides 56.4 % of households, are connected to DH. Firewood as primary fuel is used for private house heating, but it is not only inefficient but also has significant number of emissions of different gaseous and hard particle pollutants. To achieve the goals of the EU green deal, it will not be enough just to introduce non-emission technologies and transform the industrial sector. To reach EU green deal it will be important to develop all directions of the economy, including efficient use of fuels - biomass in the private house sector heat and electricity supply. If households started to replace outdated individual heating equipment in rural areas with modern wood gasification boilers with integrated electricity microgeneration equipment, it would contribute to EU climate goals and achieving climate neutrality by 2050, as well as promote rural development and population health. In this paper experimental based calculations about potential emission savings by replacing existing conventional solid biomass boilers with novel mCHP biomass boilers are presented.

kWh <sub>th</sub>	Kilowatt hours of thermal energy
Whel	Watt hours of electricity
CHP	Cogeneration
mCHP	Micro cogeneration
UN	United Nations
GHG	Greenhouse gases
EU	European union
RES	Renewable Energy Sources
DH	District heating

Keywords: climate policy; cogeneration; efficiency; emissions

#### **INTRODUCTION**

In order to highlight the topicality of the researched issue, it is important to look not only at the structure of Latvian household energy consumption, including heating consumption, but also to analyse it in the context of the European Union.

Household heating is one of the main energy consumption sectors in Europe. More than one third of total energy consumption - at the same time it changes significantly depending on changes in outdoor air temperature. There are very different types of household heating.

Northern Europe is dominated by district heating and electricity from hydropower plants. In Western Europe, it is fossil gas and electricity. In the Baltics, district heating and biomass (firewood and pellet) heating boilers. About 40 % of households in Europe are heated by natural gas, 30 % by electricity, 10 % by liquid fuels and 10 % by biomass, as well as the remaining 10 % by district heating and other technologies [1].

Heating accounts for about one sixth of European Union (EU) emissions. Although emissions from heating have fallen by almost 50 % since 1990, looking ahead to meet the Green Deal's climate neutrality targets, significant reductions in household emissions are needed in the coming years.

Liquid fuel boilers in EU households alone account for 18 million. Although more and more electricity is produced from renewable energy sources (RES), as well as opportunities appear to use biogas in gas boilers or biofuels as a liquid fuel instead of fossil fuels, it is important to promote the introduction of all the most efficient RES technologies in households.

One of the directions is heat pumps, but their widespread use requires grid flexibility, which may require significant investment in grid infrastructure, otherwise it may prove to be a bottleneck place in the development of this technology. Of course, there is great potential in the household sector for the use of solar panels and panels for heating and electricity generation, but this will also not be enough to achieve the green deal climate neutrality goals. On average, 42 % of the EU's territory is covered by forests (46 % European), with a wide range of coverage, from more than 71 % in Finland to just over 8 % in the Netherlands [2]. Therefore, the use of biomass for household heating has a wide potential not only in Latvia, but also in Europe. It is essential that modern biomass boilers ("A" class), combined with integrated Stirling engine electricity generation, not only efficiently use wood biomass for domestic heating, but also generate electricity for self-consumption and grid, thus providing electricity to households in another region.

This study addresses the issue of emission reductions in one of the sectors where this technology could be used: the replacement of existing solid biomass heating boilers with efficient biomass boilers ("A" class) together with integrated Stirling engine technology.

The aim of the study is to determine experimentally the potential reduction of GHG and PM2.5 and PM10 particulate emissions by upgrading old-generation household solid biomass heating equipment, replacing it with "A" class biomass gasification Stirling engine micro-cogeneration equipment.

## **EXPERIMENTAL**

#### Task of the experimental part

The research is planned to be based on the results obtained in experiments.

Given that most households use solid biomass (firewood) of different quality and moisture content for heating, the aim of the experiments is:

1. To determine the impact of cogeneration regime and heat energy production;

2. Not to assess the effect of fuel moisture on the heat and electricity display in the mCHP installation;

3. To determine GHG and particulate emissions from the plant operating in thermal energy and cogeneration modes.

#### **Experimental equipment**

A prototype of a solid biomass micro-cogeneration unit was used for the experiments. An "A" class [3] solid biomass heating boiler *Magasro* 31 kW [4], shown in Fig. 1. This boiler was

chosen due to the latest available technologies in the field of household biomass boilers. According to the performance characteristics of the Stirling engine [5], the boiler must be able to heat its head to at least 550 °C in order to achieve maximum engine efficiency. The technical information of the boiler manufacturer shows that the temperature of the combustion chamber can reach 800 °C, which provides the possibility to heat the temperature of the Stirling engine head inserted in it up to 600 °C, which is specified by the Stirling engine manufacturer as maximum permissible for stable engine operation [6].



Fig. 1. Solid biomass gasification boiler "A" class

In order to be able to operate the experimental unit in cogeneration mode, a Microgen Stirling engine with max. electrical output 1050W, efficiency up to 25%, (Fig. 2) [16] was integrated into the boiler, with an automated engine lifting mechanism (Fig. 3). As a result, the experimental unit (Fig. 3) can operate only in the heat energy production mode or in the cogeneration mode.



Fig. 2. Microgen Stirling engine with integrated electric generator

A schematic representation of the experimental equipment is shown in Fig. 3.



Fig. 3. Schematic representation of the experimental equipment.

For the experiments, the mCHP unit was installed in a boiler house, which provides heat energy to a small-town residential buildings. Connection to the district heating network provided an opportunity to operate the experimental equipment with maximum capacity for a long time, allowing to obtain more accurate measurement of the equipment operation. The connection diagram of the unit with the municipal district heating network is shown in Fig. 4.



Fig. 4. Drawing of the connection of experimental mCHP equipment

#### Experimental data collection and methodology

To assess the quality of the combustion process, gaseous emissions were measured using the flue gas analyser from company Testo AG, model Testo 340, which allows to determine the amount of CO2, O2, CO in the flue gas when the plant is operating in stable mode.

A Swiss company Sontex ag model Sontex Supercal 73 heat meter was used to measure the heat produced by counting heat energy given to network.

Stirling Engine Data viewer software (product of company Microgen engine corporation, engine parameter measuring software with internal sensors) was used to record Stirling engine operating parameters.

The moisture content of the wood was determined using the China company ICraft Wood Moisture Analyser iCcraft.

Determination of fine particles matter PM2.5, PM10 was performed in accordance with the method described in the standard LVS ISO 9096 "Manual determination of mass concentration of particulate matter" [7], using the particulate measuring device of Italian company TCT Teracora model Tecora Isostack G4.

To obtain experimental data, measurements were performed according to the methodology used in the study [8], [9]. In a Table 1 is described main parameters of the used biomass fuel. Experiment's ware obtained by full load of gasification chamber with wood logs with parameters mentioned in Table 1. No additional fuel was added during experiment, depending on moisture, load was variating from 15-20kg. Every 15 min. of total about 3h combustion cycle parameters ware fixed with analytical equipment mentioned at the beginning of the chapter 2.3. Summary of the produced thermal and electrical energy during hall experiment was fixed and recalculation to express results them to 1kg of fuel is shown in Fig. 6 and Fig. 7.

Exp. No.	Boiler status	Fuel	Wood logs (35-50cm) bulks
1.	Heating	Wood logs with 20 % moisture	Seasoned, mix 50% of alder and 50% stand
2.	Heating	Wood logs with 15% moisture	Dried mix 50% of alder and 50% stand
3	Heating	Wood logs with 25% moisture	Fresh cut mix 50% of alder and 50% stand
4.	СНР	Wood logs with 20 % moisture	Seasoned, mix 50% of alder and 50% stand
5.	СНР	Wood logs with 25 % moisture	Fresh cut mix 50% of alder and 50% stand
6.	СНР	Wood logs with 16 % moisture	Dried mix 50% of alder and 50% stand

Table 1. Experiment Description

7.	СНР	Wood logs with 12 % moisture	Dried mix 50% of alder and 50% stand
8.	Combined CHP/thermal	Wood logs with 12 % moisture	Dried mix 50% of alder and 50% stand
9.	СНР	Wood logs with 15 % moisture	Dried mix 50% of alder and 50% stand

## **RESULTS AND ANALYSIS OF THE EXPERIMENTAL DATA**

This chapter describes the data obtained during the experiments and their analysis.

## Heat and electricity generation

According to the task of the study, the heat energy production data were collected when the mCHP plant was operating only in the thermal energy production mode (thermal) and the plant was operating in the cogeneration mode (CHP). Heat energy generation data are shown in Fig. 5. Taking into account that combustion plants with different capacities are used in households, in order to obtain comparable data, a calculation was made for the production of heat and electricity expressed as 1 kg of fuel used.



Fig 5. Experimental results of produced thermal energy kWh<sub>th</sub> from 1kg of wood blue column for CHP and red column for thermal mode

When the unit was operating in cogeneration mode, data on the produced electricity was collected both for the unit's own consumption and given into the network. To perform the task, 9 experiments were performed, in which 1-3 experiments were performed only in the heat energy production mode, while 4, 6, 7, 9 in CHP mode, experiment 8 was performed using combination of CHP and thermal mode. The experimental results on the produced heat energy are shown in Fig. 6, while the data on the produced electricity are shown in Fig. 7.



Fig 6. Experimental results of produced thermal energy from 1kg of wood



Fig. 7. Experimental results of electrical produced from 1kg of wood and transferred to the public electric network

## Analysis of heat and electricity production data

A total of 25 experiments were performed using firewood of different moisture contents, according to Table 1. Under natural conditions, without artificial drying, the preparation of firewood with a moisture content of less than 15 % is cumbersome. A survey of market-available firewood for household consumption found that firewood with a moisture content of 20 % was the most widely available on the market [10], so for future calculations it was assumed that households use the most fuel of this quality, performing 13 experiments with firewood with 20 % moisture content.

Based on the experimental data Figure 5, the results were obtained that in cogeneration mode on average 2.84 kWh of heat energy can be obtained from 1 kg of firewood and 2.48 kWh if operating only in heat energy production mode.

When the plant was operating in cogeneration mode, the plant produced on average 0.026 kWh of electricity from 1 kg of firewood. The calculation is made by summing the equipment's own consumption 180 W and the accounting of electricity transferred to the network.

During the experiment with burning of 20 % moisture wood,  $PM_{2.5}$  and  $PM_{10}$  particle emission measurements were performed during the stable combustion process phase. Measurements were performed with the unit operating in both heat and cogeneration mode.

The results of the experiment showed that 78 mg of solid particles were emitted for the production of 1 kWh of heat energy. It was not technically possible to perform particulate measurements for all experiments, therefore their reliability was tested by evaluating data from other studies on particulate emissions from wood gasification boilers [11].

#### **Emissions data**

#### Data statistics

 $CO_2$  emissions from electricity generation are reported in different EU countries, for example, statistics for 2019 [10] show emissions, 900 g/kWh Estonia, 138 g/kWh Latvia, 65 g/kWh Lithuania. The average EU CO<sub>2</sub> emissions per kWh of electricity generation in 2019 are estimated at 287 g/kWh [12]. Taking into account the different emission levels in different countries, the EU average electricity production emission data are used for further calculations.

According to Latvian construction standards, the heat energy consumption of residential houses is allowed up to 90 kWh/m<sup>2</sup> per year [13]. The current situation in the Baltic States, which is related to heat energy consumption, is significantly worse. It is shown that in Latvia and Lithuania it exceeds 200 kWh/m<sup>2</sup> per year [14]. Most residential buildings were built before the adoption of the existing building codes, so based on the reports of energy audit data collection [15], [16], it can be concluded that in fact the heat consumption of households exceeds the permissible level of building standards. According to these reports, it averages at least 150 kWh/m<sup>2</sup> per year. For future calculations, we use these data as the total heat consumption of households, which also includes the energy required for hot water preparation.

According to statistical data, the average household size in rural areas of Latvia, where firewood is mostly used for heating, is 93.9 m<sup>2</sup> [17]. It is taken into account that this value is the average size of households, which also includes buildings without district heating, the area of which is below average. For further calculations, in this study the minimum heating area is taken to be 200 m<sup>2</sup>, as this area is recommended in the technical documentation of the boiler manufacturer [4].

#### CO<sub>2</sub> emissions from heat and electricity production

According to previously accepted data on household size and average heat energy consumption, it is determined that a household with a heated area of  $200 \text{ m}^2$  consumes 39 MWh of heat energy during a calendar year.

 $CO_2$  emission tests were performed with the plant operating in heat and cogeneration mode. The data were obtained using a *Tecora Isostack G4* test rig, measuring a flue gas flow of 5.99 m<sup>3</sup> for burning 1 kg of wood. During the recalculation, it was determined that 500 g of  $CO_2$  emissions are generated to produce 1 kWh of thermal energy. Taking into account that on average 2.53 kWh<sub>th</sub> was obtained from burning 1 kg of wood (Fig. 6), we obtain that the household emits an average of 7707.51 kg of  $CO_2$  for heat energy production.

According to the experimental results in Fig. 7, we calculate that when the plant is operating in cogeneration mode, 1014 kWh of electricity would be produced per year.

According to the accepted data on  $CO_2$  emissions from electricity generation [12] and the amount of electricity produced during the year, we obtain that the annual reduction of  $CO_2$  emissions of a household would be 291.02 kg.

#### Particulate emissions

In the measurement of particulate emissions, according to the methodology described in Section 2.3, it was determined that 78 mg of particulate matter is emitted for the production of  $1 \text{ kWh}_{\text{th}}$  (Table 2).

Calculating household particulate matter emissions results in 304.20 kg of particulate matter emissions per year.

Table 2. Fine particle and CO<sub>2</sub> Emission measurement results from kWh<sub>th</sub> production

Exp. No.	Parameter	Unit	Measurement
1.	CO <sub>2</sub>	g	500
2.	Fine particles	mg	78

## Analysis of experimental results to determine potential reductions in particulate matter and GHG emissions

When compiling data on  $CO_2$  emissions, taking into account the emissions from heat production in the experimental installation during the year (Fig. 8(2)), they are compared with the emissions from the old type boilers (Fig. 8(1)) [7], [9],



Fig. 8. Comparison of GHG emissions from average household using old biomass boiler (1), novelle Stirling engine based mCHP boiler (2)

As shown in Fig. 8, the annual  $CO_2$  emission reduction of one household, using the parameters adopted in Section 3.2.1 of the study, using the Stirling engine mCHP device reaches 7840.60 kg CO<sub>2</sub> reduction. Given that both new and old boilers use biomass, they can both be considered as  $CO_2$  neutral, thus, the comparison shown in Fig. 8 only shows the differences in their operating efficiency.

To determine the reduction of gaseous emissions, we use data on the electricity produced by the mCHP unit, which it is able to produce during the year by replacing the electricity received from the network. Taking into account the calculation method described in Section 3.1, we obtain that the annual reduction of CO<sub>2</sub> emissions reaches 291.02 kg.

The results of particulate emission measurements are presented in Table 2. For old generation biomass boilers, particulate emissions are assumed to be 417 mg kWh<sub>th</sub> [18].

The results of calculation the potential reduction in particulate emissions over one year if the manual biomass boiler were replaced by the Stirling engine mCHP analogue used in the experiment is shown in Fig. 9.



Fig. 9. Comparison of fine particle emissions from average household using old biomass (1), novelle Stirling engine based mCHP boiler (2) per year calendar

The total annual reduction in particulate emissions is 13221 kg (Fig. 9).

#### DISCUSSIONS

Our research was based on comparison of the literature observation and the data obtained in the practical part of the experiments.

The experiments were designed so that their results could be compared as accurately as possible with the real conditions in households, thus it was chosen to use different quality fuels in the experiments, similar to what was done in the research [7], [9]. When operating the heating unit in the micro-cogeneration mode, the optimal fuel moisture level and heat load were determined. The main focus of the study was on the possibilities of reducing GHG emissions, thus the conditions under which the heating plant emits the least GHG and particulate matter were also studied. It was determined that for maximum power generation it is necessary to reach the Stirling engine head temperature of 8001000 °C, at which the power generation capacity is in the range of 700-900 W, but not all experiments managed to reach such engine head temperature is achieved under the ideal combustion conditions allowed by a combustion plant of this design. In the emission calculations was only that data, which got repetitions in the experiments. The levels of GHG and particulate emissions in the maximum energy production modes did not show significant differences compared to the optimal conditions.

## CONCLUSIONS

The study made it possible to compare both the total fuel consumption of households and the emissions that could be reduced if old heating equipment were replaced by similar equipment used in the study. The reduction of GHG emissions from one household during a calendar year was calculated to be 291.02 kg, which was determined by the amount of electricity produced, which replaces the electricity received from the grid.

The overall reduction in GHG emissions is shown in Fig. 8, this comparison is more indicative, showing fuel efficiency, as biomass heating installations are considered to be  $CO_2$  neutral.

The potential reduction of particulate matter from one household per year was determined to be 13221 kg if the old generation heating equipment were replaced with the analogue of the equipment used in the experiments.

A reduction in heat and electricity production was observed using fuels with a higher moisture content. The optimal fuel moisture content was determined to be 20%, at which the highest heat and electricity generation was found. Using fuels with a lower moisture content, i.e. below 15%, a decrease in heat and electricity generation was observed. The reduction can be explained by the design features and automation settings of the researched equipment, which limit the temperature regime in the gasification and combustion chamber of the equipment, limiting the maximum temperature in the convective part of the boiler, prematurely shutting off the air supply. This reduces the temperature in the combustion chamber, preventing the Stirling engine head from heating to the desired temperature.

The results of the study were obtained, which indicate the positive impact of the cogeneration regime on heat energy production. The highest efficiency was detected with 15% of moisture content wood (Fig. 5). Average efficiency of thermal energy production increase from CHP regime was about 12.88%.

When studying the emissions of particulate matter, it was concluded that they are larger in the initial and final phase of operation of the heating plant but are constant when the plant is operating in a stable mode.

No change in particulate emissions was observed when the plant was operating only in thermal energy or cogeneration mode.

The installation of such equipment in households would reduce household emissions by replacing electricity from the grid.

The cogeneration mode has a positive effect on the overall thermal energy efficiency of the plant, which reduces fuel consumption, thus reducing household heating emissions.

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# PRODUCTION OF BIOFUELS FROM HYDROTHERMALLY PRETREATED SEWAGE SLUDGE USING ZYMOMONAS MOBILIS

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#### EXTENDED ABSTRACT

#### **INTRODUCTION**

Sewage sludge is a by-product of urban wastewater treatment and its generation has increased dramatically, from 10.106 to 13.106 dry metric tons per year, between 2010 and 2020 in the European Union [1,2]. The management of this waste represents one of the main disadvantages in Wastewater Treatment Plants (WWTPs) due to its low solid concentration, high organic load and the presence of potentially dangerous compounds, such as heavy metals, persistent organic pollutants and pathogenic organisms [3]. This implies a challenge in operational and economic terms since the cost associated with the treatment and disposal of the sludge represents approximately 50% of the total operating cost of WWTPs [4]. Traditionally, different methods have been used for the management of activated sludge, such as landfilling, soil/land application (with or without previous composting), incineration and anaerobic digestion [5]. However, the pollution problems that the sludge can generate, as well as its high moisture content, and the tightening of environmental regulations hamper the efficient and economic application of some of the treatments [3]. Therefore, it is essential to promote a new growth model, based on circular economy, which focuses on the valorisation of wastes in order to use resources efficiently. In this sense, it is possible to achieve efficient management of sewage sludge through specific techniques, such as hydrothermal treatments (thermal hydrolysis and wet oxidation) coupled with fermentation processes, thus increasing the supply of clean, renewable and sustainable energy.

#### **METHODS**

In this study, fermentations were carried out using *Zymomonas mobilis* CECT 560 for the production of biofuels from secondary sewage sludge after being subjected to hydrothermal treatments. To this end, thermal hydrolysis (TH) and wet oxidation (WO) were carried out at different pressure and temperature conditions, concluding that the best ones were 170 °C and 40 bar. The fermentation processes were carried out with both the oxidised and the hydrolysed sludge, the initial glucose concentration being 10 g/L in both cases. The evolution of the fermentations with the hydrothermally pre-treated sewage sludge were monitored by means of bacterial growth, consumption of substrate (glucose) and the production of bioethanol. In addition, the concentrations of possible fermentation inhibitor compounds, such as phenolic compounds, furfural, hydroxymethylfurfural (HMF) and organic acids were evaluated.

#### RESULTS

Regarding the performance of the oxidised and hydrolysed sludge as fermentation media, it was observed that glucose was totally consumed in the hydrolysate liquid in 24 h. However, in the case of the oxidised liquid, the consumption of the substrate was only partial. In fact, only 53% of glucose was consumed after 36 h. Besides, cell growth showed that the maximum optical density in the hydrolysate was 0.9 at 48 h, whereas in the oxidised one, the maximum value (0.3) was achieved after 10 h and remained stable from this time onwards. This showed that the oxidised liquid is a more toxic medium for *Zymomonas mobilis* growth. In relation to the production of ethanol, it was found that the maximum production was obtained in 48 h in the hydrolysed liquid with a yield of 78% of the theoretical one [6]. In the oxidised liquid, the yield obtained was only 27% of that expected. This delay and decrease in glucose consumption, as well as cell growth and ethanol production, were observed in both the hydrolysed and oxidised liquid when it was compared with the pure culture media. This behaviour can be explained due to the presence of several inhibitory compounds. For this reason, the content of phenolic compounds, furfural, HMF and organic acids present in the sewage sludge after WO and TH

was analysed. The organic acids determined were non-volatile hydroxy (oxalic, malic, maleic, lactic) and volatile acids (formic, acetic and propionic).

The concentration of each of the fermentation inhibitor compounds for both the hydrolysed liquid and the oxidised one is presented in Fig. 1. The concentration of phenolic compounds in the oxidised liquid was 237 ppm, while in the hydrolysed liquid was 470 ppm. For furfural, the concentration was similar in both cases, the value being 32 ppm in the oxidised and 27 ppm in the hydrolysate. On the other hand, the HMF concentration in the oxidised was 9 ppm, while in the hydrolysate was 5 ppm. The concentration of organic acids was significantly higher in the oxidised (5372.4 ppm) than in the hydrolysate (1418.3 ppm).



Fig. 1. Concentration of fermentation inhibitor compounds in the sewage sludge after WO and TH. Phenolic compounds (**■**), furfural (**■**), HMF (**■**), organic acids (**■**).

#### CONCLUSIONS

Hydrothermal treatments, such as WO and TH, can be considered interesting techniques for the solubilization of sewage sludge in order to be used as fermentation media for the production of biofuels. Regarding anaerobic fermentations with *Zymomonas mobilis* CECT 560, it was proved that the best results were achieved with the hydrolysed one, since 4.3 g/L of ethanol were generated after 48 h of fermentation, whereas with the oxidised one, the maximum ethanol concentration was 1.6 g/L after 36 h. This behaviour can be explained due to the concentration of fermentation inhibitor compounds, specifically organic acids, which was around 4 times higher in the oxidised liquid than in the hydrolysed one. Therefore, high yields of biofuel production from hydrothermally pre-treated sewage sludge will depend on the operational strategy used, as it determines the availability of fermentable sugars and the concentration of inhibiting compounds.

Keywords: activated sludge, bioethanol, fermentation, inhibitory compounds, thermal hydrolysis, wet oxidation

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# CHARACTERIZATION OF PELLET PRODUCTS FROM DIFFERENT LIGNOCELLULOSIC BIOMASS IN TURKEY

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#### ABSTRACT

Fossil fuels such as petroleum and coal is still the most used resource of energy in the world. While the need of energy is increasing, it becomes an important issue to supply it from sustainable and renewable sources such as forest, industrial, and agricultural waste. Increasing consumption of fossil fuels are not only a problem but also an important problem of global warming as well as environmental pollution. Biomass energy becomes an alternative energy to meet the increasing energy demand and to reduce global warming effect. Biomass can be obtained from various raw materials such as forest residues, wood, agricultural waste, annual plants, and chemically untreated wood industry residues. On the other hand, pellets or briquettes manufacturing have many advantages such as increasing density and burning efficiency of the waste and reducing transport cost. It decreases also carbon footprint along with supporting circular economy.

This study aims to determine the quality of wood and non-wood pellets according to EN ISO 17225-2 and EN ISO 17225-6 standards and the obtained pellets were characterized by Fourier transform infrared spectroscopy (FTIR-ATR). The elemental composition of the wood pellet and non-woody pellet samples were determined using Inductively Coupled Plasma Mass Spectrometry (ICP-MS). The pellet samples were obtained from various pellet factories in Turkey, and the pellet samples were analysed to determine some chemical and mechanical properties.

It is clear that woody pellets even in different types of wood species and ratios ensure the standard requirements. But, FB and T1 do not meet the standard requirements in some aspects.

Keywords: Bioenergy, Pellet, FTIR-ATR, Elemental analysis, Ash melting behaviour, Mechanical durability.

## **INTRODUCTION**

Energy consumption is increasing rapidly due to factors such as increasing world population, industrialization, urbanization, and rising living standards in recent years and energy resources continue to be depleted rapidly. Most of the energy resources used in the world are obtained from fossil sources such as oil, coal, and natural gas. In addition to the depletion of these fossil resources in the future, it will bring negative effects such as global warming, temperature changes, climate changes, increased carbon emissions, and environmental pollution. Biomass energy is one of the energy sources that can meet the increasing energy demand in a sustainable way and environmentally friendly. In addition, the use of lignocellulosic materials in energy is increasing day by day with the aim to reduce carbon emissions having impact on global warming [1].

Pellet manufacturing is the feasible way to use biomass waste to obtain clean energy. Among the advantages of pelleting biomass are increasing density and burning efficiency of the waste and reducing transport cost. Biomass is renewable and clean resource, can be grown everywhere, has storage capacity, use of biomass energy causes less greenhouse effect compared to other fossil sources, does not cause acid rain, supply  $CO_2$  balance in the atmosphere, decreases fossil fuel use, provide financial savings, for rural areas. Due to these

advantages, energy production, chemical production, fuel production, and electricity generation are carried out using biomass resources. The composition of biomass material involves a complex mixture of various organic compounds and polymers. Hemicellulose, cellulose, and lignin are the basic building blocks of biomass. The properties and proportions of these lignocellulosic materials differ according to the type of biomass. Materials with a lignocellulosic structure (wood, tea, hazelnut, straw, etc.) represent important renewable resources [2,3,4].

Gunduz et al. in their study, produced pellets from three different wood species (*Rhododendron ponticum, Laurus nobilis, and Castanea sativa*). They determined the elemental analysis and characterization of the woody pellets. As a result of the study, it was found that the bulk density shows similar results, the chestnut wood pellets contain lower ash content, the moisture content is below the limits defined under standards EN 14961-2 and DIN 51731, the higher elemental analysis values of the oven-dried pellets and the higher calorific values of the woody pellets were obtained [5].

Chandrasekaran et al. compared the chemical properties and energy values of wood pellets and wood chips using several standards (CEN/TS, Austrian, German, Swedish, PFI(U.S.)). They analysed 23 wood chips samples and 132 wood pellet samples. As a result, they found that some pellet samples had high concentrations of heavy metals, and contaminated wood or pressure-treated wood might not meet these standards [6].

The other study evaluated the production of biomass pellets from vineyard wastes. They evaluated the elemental analysis and energy values of the non-woody pellets made according to EN ISO 17225-6. The findings stated, which vineyard wastes can be used for energy; the copper content in some pellet types is at limit values, heavy metals are below the limit values, and high-quality pellets can be produced [7].

Picchio et al. examined the quality of pellets produced from woody and non-woody raw materials. They stated that woody pellets are of higher quality than non-woody pellets, that some non-woody pellets have improved their quality properties as a result of blending with woody pellets, and recently torrefaction studies have increased quality, and the use of binding agents make possible method to ensure quality [8].

Miranda et al. (2020) investigated pellets obtained from different sources. They performed the analysis of ten kinds of laboratory-made pellets from different raw materials. The result was achieved as follows: higher C content increases the calorific value; pine pellets are more preferred in the market due to lower ash content; it is difficult to meet EN ISO 17225 standard specifications by some types of biomass; combustion systems are important; different types of pellets produced according to EN ISO 17225 will contribute to environmental success [9].

Brand et al. investigated pellets in different blends from agricultural and wood waste and their effects on quality. They blended rice and pine samples and evaluated the quality according to EN ISO 17225. The achieved results showed that the mechanical strength is not affected by the mixture of rice and pine in the compositions; the ash content increases with the addition of the mixture, and meets the standards when mixed with pine [10].

Pegoretti Leite de Souza et al. investigated the effect of lignine distribution and physicochemical properties on the quality of different types of pellets. They performed mechanical, chemical, and physical analyses for 4 different samples: *Pinus radiata, Eucalyptus nitens, Paulownia elongara* A server, and *Miscanthus A giganteus*. They found that *Pinus radiata* is more suitable for pellet production and has high calorific value, anatomical structure is important for pellet quality, miscanthus giganteus pellets contain high ash [11].

Christoforou and Fokaides studied the thermochemical properties of pellets obtained from agricultural and industrial waste. They analysed 8 different pellet samples according to EN ISO 1725-2 and EN ISO 17225-6. As a result, they found that blends of exhausted olive husk, mulberry tree pruning and grape pomace (85% by volume), and chemically untreated wood shavings (%15 by volume) with high ash content, exhausted olive husk had high nitrogen content, and the resulting pellets had high calorific values [12].

This study aims to reveal some of the quality characteristics of woody and non-woody pellets obtained from different locations in the market of Turkey.

## MATERIALS AND METHODS

The pellet samples were commercially obtained from various pellet factories in Turkey. Of these pellet samples were 9 woody and 2 non-woody (tea and hazelnut) pellets. All pellet samples were ground according to TAPPI T257 cm-85 standard for mechanical test, elemental analysis, FTIR analysis and some chemical analysis. The pellets were identified as seen at Table 1. Pellet samples also are shown in Fig. 1.

Sample Code	Sample Name
T1	Tea tree waste
H1	Hazelnut shell
FB	Fiber Sludge
W1	Pinus and Oak blend
W2	Pinus and Oak blend
W3	Pinus and Beech blend
W4	Pinus and Oak blend
W5	Softwoods and Hardwoods blend
W6	Pinus and Beech blend
W7	Pinus and Oak blend
W8	Pinus and Oak blend

Table	1:	Identification	pellet	samples



Fig. 1: Some of the woody and non-woody pellets

Before analyses pellet samples were ground by the Wiley mill. Analyses were performed according to test standards as below:

- Moisture content was determined according to TAPPI T 412 om-94.
- Ash content was determined according to TAPPI 211 om-85.
- ICP-OES Analysis

Pellet samples were primarily ground in Wiley-type mills. The powdered samples were dried at 55-60 °C for 24 hours for the use in elemental determination. 0.5 g of oven-dried samples were weighed and placed into teflon tubes produced for the use in the microwave device. 5 ml of concentrated nitric acid (NHO<sub>3</sub>) was added to the weighed samples. After maintaining for 10 minutes, 1 ml of hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) was added. Later, the samples were dissolved in Berghof Speedway 4 microwave-digested. The solutions were filtered through blue band filter paper and ultrapure water was added to 50 ml.

Element determination experiment with ICP-OES was performed on PerkinElmer Optima 7000 DV device. The device was run for 15-20 minutes before starting analysis. The solutions containing 5 different concentrations of the elements to be analysed were prepared and the device was calibrated. After the device was calibrated, approximately 10-12 ml of sample solutions were taken and transferred to 15 ml tubes and the analysis process was carried out on the device. According to EN ISO 17225-2, EN ISO 17225-6, 9 elements determination are required in the samples. These elements are Cr (chromium), Pb (lead), Zn (zinc), S (sulfur), As (arsenic), Cd (cadmium), Hg (mercury), Ni (nickel), Cu (copper) [13].

• Fourier transform infrared (FTIR) Analysis

Fourier transform infrared absorption data was obtained using a FTIR spectrometer (PerkinElmer 100 FTIR spectrometer; PerkinElmer Inc., Bridgeport, CT, USA) combined with an attenuated total reflection (ATR) unit (The Universal ATR Accessory (UATR-PerkinElmer Exlusive); Bridgeport, CT, USA)) at a resolution of 4 cm<sup>-1</sup> for 32 scans in a spectral range of 600 cm<sup>-1</sup> to 4000 cm<sup>-1</sup>. Specimens were milled and passed through an 80-mesh sieve, and the analyses were performed on ground specimens. The spectra were baseline corrected and normalized to the highest peak. The FTIR spectroscopy was improved using an ATR unit that provided direct interaction of the measuring beam with the sample and reflection of the attenuated radiation to the spectrometer, and increased the sensitivity of FTIR-based analyses [14].

- Ash melting behaviour was determined according to CEN/TS 15370-1 (2006).
- Mechanic durability was determined according to ISO 17831-1 (2015).
- Bulk density was determined according to ISO 17828 (2015).

## **RESULTS AND DISCUSSION**

Mechanical durability, bulk density, moisture content, and ash content of the pellet samples are shown in Table 2 according to EN ISO 17225-2 standard. There are no samples of analysis of FB (Fiber sludge) and H1(Hazelnut shell) pellet in Table2.

The blending status of W1, W2, W4, W7, and W8 samples are consisting of same wood species which are Pinus and Oak but blends ratios are not known, so interpretation could be made according to the results obtained, and accordingly, mechanic durability of W1 is the lowest and W4 is the highest.

The results of the study showed that the bulk density of all pellets meet the requirements of EN ISO 17225-2 and EN ISO 17225-6 standard which define the lowest acceptable value of  $600 \text{ kg/m}^3$ . The highest bulk density belongs to W3 sample could be attributed to the highest oak content among all blends.

W8 pellet sample has the highest ash content among woody pellets. The high ash content of W8 may be due to the presence of bark waste.

When comparing mechanical durability of tea tree waste to that of woody pellets, it is obviously seen that the tea tree waste has shown the lowest value, besides inorganic substances are shown the highest value.

The non-woody T1 sample was evaluated according to EN ISO 17225-6 and given in Table 2 with the other pellets.

EN ISO 17225-2						Pe	ellet S	ample	es' An	alysis	Resu	lts	
Property Class	Unit	A1	A2	В	W1	W2	W3	W4	W5	W6	W7	W8	T1*
Mechanic durability, MD	w-%	MD ≥97,5	MD ≥97,5	MD ≥96,5	96,5	97,9	97,3	98,3	97,3	98,7	97,5	96.9	86,1
Bulk density, BD	kg/m <sup>3</sup>	BD ≥600	BD ≥600	BD ≥600	600	640	796	700	640	690	640	650	630
Moisture content	w-%	M10 ≤10	M10 ≤10	M10 ≤10	7,86	2,77	5,89	6,79	7,29	7,97	8,86	6,01	6,93
Ash content	w-%	A0.7 ≤0,7	A1.2 ≤1,2	A2.0 ≤2,0	0,89	0,90	1,57	1,46	1,02	0,94	1,56	1,99	5,75

Table 2. C	Duality values	according to ]	EN ISO	17225-2 or	EN ISO 17225-6
1 abic 2. C	Juanty values	according to 1		$1/22J^{-2}$ OI,	$L_1 100 17225-0$

W1- Pinus and Oak mix, W2- Pinus and Oak mix, W3- Pinus and Oak mix, W4- Softwoods and Hardwoods mix, W5- Pinus and Oak mix, W6- Softwoods and Hardwoods mix, W7- Pinus and Oak mix, W8- Pinus and Oak mix, T1- Tea.

\*According to EN ISO 17225-6.

The Ash melting behaviour of pellet samples is given in Table 3 according to CEN/TS 15370-1. There are no samples of analysis of FB (Fiber sludge) and H1(Hazelnut shell) pellet samples in Table 3.

The deformation temperature of woody pellets varies by 1.5% in between the lowest and the highest temperature values. The deformation temperature of tea tree pellet has the highest value, and it can be thought that arising from its chemical components.

As it is seen in Table 3, the shrinkage temperature value is the lowest at tea pellet and it is thought that the volatile extractive components are probably more in this sample. This shrinkage could be due to a number of factors, including the liberation of carbon dioxide, volatile alkali compounds, and sintering [15].

Ash melting behaviour, CEN/TS 15370–1					Pellet Samples' Analysis Results								
Property Class	Unit	A1	A2	B	W1	W2	W3	W4	W5	W6	W7	W8	T1
Shrinkage starting temperature	°C	-	-	-	1225	1190	1020	1270	1040	1251	1219	1248	640
Deformation temperature	°C	≥ 1200	≥ 1100	-	1213	1220	1190	1245	1190	1242	1216	1246	1300
Hemisphere temperature	°C	-	-	-	1233	1230	1240	1279	1250	1258	1222	1251	1370
Flow temperature	°C	-	-	-	1273	1240	1250	1286	1260	1261	1237	1262	1380

Table 3: Ash melting behaviour of the pellet samples

Elemental analyses were performed according to EN ISO 17225-2, EN ISO 17225-6 to determine the commercial pellets characterization and the quality value obtained. It has been observed whether these products meet the standards described as fuel energy in a manner that will not harm the environment.

Regarding elemental analysis results, the content of S, Cd, Ni, Zn, Cu, Pb, Cr, As, and Hg in woody pellets (W4, W6, W7, and W8) are within EN ISO 17225-2's limits. Furthermore, the non-woody H1 pellet's element results are also within EN ISO 17225-6's limits.

The heavy metal content of FB pellet is above acceptable limits according to EN ISO 17225-6 standard and it is thought that fiber sludge cannot be used as pellet for domestic areas, and this sludge could be used in thermochemical processes such as electricity generation, synthesis gas.

Table 4 shows elements values of S, Cd, Ni, Zn, Cu, Pb, Cr, As, Hg of pellets. There are no samples of elemental analyses of W1, W2, W3, W5, T1 pellet samples in Table 4.

Specification	Units	EN ISO 17225-2	FB	W7	W8	W6	W4	H1
S	w-% dry	0.04<0,04	25,84	<0,04	<0,04	<0,04	<0,04	<0,04
Cd	mg/kg	$\leq 0,5$	0.061	0.022	0.034	0.109	0.09	< 0.5
Ni	mg/kg	$\leq 10$	12.46	0.751	0.685	0.909	1.45	0.601
Zn	mg/kg	$\leq 100$	113.6	6.824	8.394	6.348	7.221	4.67
Си	mg/kg	$\leq 10$	12.89	0.845	0.814	1.313	1.751	3.33
Pb	mg/kg	$\leq 10$	0.469	0.405	0.503	1.851	0.591	0.128
Cr	mg/kg	≤10	6.165	0.857	0.939	0.542	1.774	0.633
As	mg/kg	$\leq 1$	0.623	< 0.05	< 0.05	0.346	0.137	< 0.05
Hg	mg/kg	$\leq 0,1$	< 0.01	< 0.01	< 0.01	0.016	0.176	< 0.01

Table 4: Elemental Analysis Results of the Wood Pellets

The characterization of biomass in its natural state has been an important problem for its users and commercial implementers. Sometimes it might be very important to have knowledge

about the content of biomass pellets as quickly as possible. Since destructive techniques can be very time-consuming, the application of IR spectroscopy may help to understand the chemical structure of biomass. The IR spectra of agricultural-based pellets and wood-based pellets are shown in Fig. 2 and 3. "The most important bands are observed in the so-called 'fingerprint' region between 1800 cm<sup>-1</sup> and 650 cm<sup>-1</sup>" [14]. The identification and explanations of the IR peaks are presented in Table 5 and 6. The peaks are defined with reference to literature reports [14,16-19]. Naturally, there are some differences in the bands of spectra observed in this study compared to reports in the literature since the woody samples are mixtures of softwood and hardwood and some small amounts of bark and fiber sludge is containing some different chemicals such as adhesives. So, it is not possible to match the IR bands of the samples in this study with literature. However, it was apparently observed that all samples have the most important bands of lignocellulosic as seen in Table 5 and 6.

As shown in Fig. 2, there are no considerable differences between spectra for hazelnut (1) and tea tree waste (2) except the band at  $1732 \text{ cm}^{-1}$  and the band at  $1728 \text{ cm}^{-1}$  wavelengths respectively. The band at  $1732 \text{ cm}^{-1}$  represents xylan for hazelnut and at  $1728 \text{ cm}^{-1}$  for tea tree waste as seen in Fig. 2.



Fig. 2: IR Spectra of hazelnut or tea tree waste pellets.

Table 5: The numbers in pare	enthesis indicate peak	numbers which were s	shown in Fig. 2.

Wavenumber	Band assignment	Specimens
(cm <sup>-1</sup> )		
1732 (1)		H1
1728 (1)	C=O stretching in xylans (unconjugated)	T1
1691 (2)	H-O-H deformation vibration of absorbed water and C=O	T1
	stretching in lignin	
1605 (3)	Aromatic skeletal vibrations + C=O stretching S≥G	T1, H1
1512 (4)	A remetie sheletel with stiens in light	T1
1507 (4)	Aromatic skeletal vibrations in lighth	H1
1441 (5)	CIL deformation withoutions in lignin and walon	T1
1436 (5)	CH <sub>2</sub> deformation vibrations in lighth and xylah	H1

1421 (6)	Aromatic skeletal vibrations combined with C-H in plane deformation + C-H deformation in lignin and carbohydrates	H1
1370 (7)	C. II. deformation in callulate and hemicallulate	H1
1362 (7)	C-H deformation in centrose and nemicentriose	T1
1317 (8)	C-H vibration in cellulose + $C_1$ -O vibration in syringyl derivatives	T1, H1
1233 (9)	Acetyl and carboxyl vibrations in xylan and C=O stretching vibrations in lignin	T1, H1
1140 (10)	C-O-C vibration in cellulose and hemicellulose	T1, H1
1026 (11)	C=O stretching vibration in cellulose, hemicelluloses and lignin	H1, T1
895 (12)	C-H deformation in cellulose	H1, T1
814 (13)	C-H deformation in cellulose	H1, T1

References are practiced on literature such as Harrington *et al.* 1964; Faix 1991; Pandey 1999; Dogu *et al.*2017; Mertoglu Elmas and Yilgor 2020. Some of the bands of the spectra in this work differ from literature values since their nature and composition. Same references are used for woody and agricultural samples [14, 16-19].

On the other hand, the differences are more distinct in woody pellets spectra as can been seen in Fig. 3. Especially fiber sludge (FB) differs in its contents dissimilarity (Fig. 3). The band observed at 1541 cm<sup>-1</sup> can be referred to as amine groups which represent the existence of formaldehyde polymerization in the sample. Even though the samples W1, W2, W3, W4, W5, W6, W7, and W8 contain both softwood and hardwood, differences in spectra may come from the ratios of the hardwood and softwood contents in the pellet samples.



Table 6: The numbers in	parenthesis indicate	peak numbers which	were shown in Fig. 3.

Wavenumber	Band assignmen	t	Specimens
(cm <sup>-1</sup> )			

1740(1)		W/1
1740(1) 1722(1)	C-O stratching in vylans (unconjugated)	$W_1$ $W_2$ $W_6$ $W_4$
1732(1) 1724(1)	C=O stretching in xyrans (unconjugated)	$W_{2}, W_{0}, W_{4}$
1/24(1)		W2, W7, W8, W3
1691 (2)	H-O-H deformation vibration of absorbed	W1 W2
1649 (2)	water and C=O stretching in lignin	W2
1631 (2)		FB
1608 (3)		W3
1605 (3)	Aromatic skeletal vibrations $+ C - O$ stretching	W4, W8, W5
1595 (3)	S>G	W7
1591 (3)	5_0	W1, W6
1577 (3)		FB
1510 (4)		W1
1508 (4)		W3, W4
1507 (4)	Aromatic skeletal vibrations in lignin	W5, W2, W6, W7, W8
1504 (4)		FB
1462 (5)		FB
1453 (5)	CH <sub>2</sub> deformation vibrations in lignin and xylan	W1, W6, W4 W7
1448 (5)		W8
1423 (6)		W2 W3
1423(0) 1422(6)	Aromatic skeletal vibrations combined with C-	W1 W6
1422(0) 1421(6)	H in plane deformation + C-H deformation in	$W_1, W_0$ $W_5, W_4, W_7, W_0$
1421(0)	lignin and carbohydrates	W 3, W 4, W 7, W 8
141/(6)		FB
13/0(7)	C-H deformation in cellulose and	W1
1368 (7)	hemicellulose	W3, W6
1365 (7)		W2, W4, W5, W7, W8
1324 (8)		W6
1321 (8)	$C_{-}H$ vibration in cellulose + $C_{1-}O$ vibration in	FB
1316 (8)	svringyl derivatives	W3, W5
1315 (8)	synngyr denvauves	W1, W4
1314 (8)		W2, W7, W8
1262 (9)		W2
1260 (9)		W4, W5
1259 (9)	Acetyl and carboxyl vibrations in xylan and	W1, W8
1256 (9)	C=O stretching vibrations in lignin	W7
1239 (9)		W3
1236 (9)		FB, W6
1161 (10)		W5
1157 (10)	C-O-C vibration in cellulose and hemicellulose	W1 W3 W4 W6 W7 W8
1148 (10)		FR W2
1108 (11)		W7 W8
1100(11) 1105(11)		$\mathbf{FR} \mathbf{W} 1 \mathbf{W} 2 \mathbf{W} 4 \mathbf{W} 5$
105(11) 1052(11)	C-O-C vibration in cellulose and hemicellulose	$W_2 W_5$
1033(11) 1050(11)		
1030 (11)		
1029 (12)	C=O stretching vibration in cellulose and	FB, W1, W4
1026 (12)	hemicellulose	W2, W3, W5, W6, W7, W8
896 (13)	C-H deformation in cellulose	W1, W2, W4, W5, W7, W8
894 (13)		

References are practiced on literature such as Harrington *et al.* 1964; Faix 1991; Pandey 1999;Dogu *et al.*2017; Mertoglu Elmas and Yilgor 2020. Some of the bands of the spectra in this work differ from literature values since their nature and composition [14, 16-19].
## CONCLUSIONS

In this study, the pellets produced commercially in Turkey were studied to identify the quality characteristics of these pellets in the current situation.

In conclusion, it was determined that W1, W3, W4, W5, W7, W8 pellet samples meet the B quality class requirements, while W2 and W6 pellet samples meet the A2 quality class requirements, according to EN ISO 17225-2. Besides, it is determined that T1 pellet qualification does not meet EN ISO 17225-6 quality standard because of its very low mechanical durability, and FB sample would not be used in domestic areas due to containing heavy metals higher than EN ISO 17225-2.

It is clearly seen that woody pellet samples meet the standard requirements even though containing different wood species and ratios.

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# FIBROUS HEMP BIOMASS USAGE FOR ENERGY PURPOSES AND BIOMASS ASH SUSTAINABLE UTILIZATION

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#### EXTENDED ABSTRACT

### **INTRODUCTION**

Fibrous hemp has high potential to increase the share of renewable energy. In many countries, e.g., in the China, Canada, USA, Ireland, Spain, Germany, Poland, Sweden hemp biomass is use for energy purposes [1,2]. Hemp exhibits many salient features like low feedstock cost, high biomass content, high land use efficiency, higher dry matter (DM) yield, low nutrients requirement, no/zeropesticide demand and can improve soil health with organic matter [3]. Research shows, as a solid fuel, the adjusted biomass energy yield of hemp is equal to or higher than that of other conventional energy crops [1]. About 10 tons of hemp biomass from one hectare can be used for energy purposes [4].

Use hemp for energy purposes is relatively new and comprehensive research into the preparation and use of biofuels is needed. This paper analyses the preparation of fibrous hemp biomass for solid fuels.

The amount of biomass ash (BA) generated worldwide will likely continue to increase in the near future [5]. Although biomass ash has a potential beneficial use in soil or other products, this residue is still largely landfilled [6]. For a sustainable use of biomass it is important to recognise that the ash can largely be returned to the soil, renewing and replacing the extracted nutrients, especially P and K [7,8]. Returning of biomass ash as fertilizer to field plays great role in sustainable utilization of biomass as energy [9]. The use of biomass ash as fertilizer requires detailed research with long-term monitoring of the impact on soils [10].

### MATERIALS AND METHODS

There were investigated three varieties of fibrous hemp e Felina 32, USO 31 and Finola. In the Upytė experimental station (Lithuanian Research Center of Agriculture and Forestry) fibrous hemp was grown for fiber. Investigations were carried out in the fields and laboratories of Vytautas Magnus University Agriculture Academy (VMU AA) in 2017–2020. In the Institute of Agricultural Engineering and Safety were investigated the technological-technical means of these plants processing, biofuel pellet production and usage for energy purposes. These investigations takes place in stages – firstly, the grown plants are crushed and milled; the flour is pressed into pellets; the pellets are burned, and heat energy and ash are obtained; then, the ash is used for fertilization.

In the Lithuanian Energy Institute (LEI) the parameters of the granules thermal properties, such as calorific value, elemental composition and ash content were evaluated.

The investigations of physical-mechanical and thermal properties of fibrous hemp granules, determination of melting and chemical composition of ash were performed according to the standard methodology valid in Lithuania and the European countries.

#### RESULTS

To substantiate the suitability of fibrous hemp for biofuel, there were investigated the physicalmechanical and thermal properties of fibrous hemp (Felina 32, USO 31, Finola) biomass, which was pressed into cylindrical granules.

Results of investigated fibrous hemp pellets characteristics have shown that as the moisture content of pellets increases, their density decreases. The density of the produced  $10 \pm 2\%$  moisture biofuel pellets

showed that the highest density of pellets were obtained by pressing fibrous hemp "USO 31" granules  $-1285.7 \pm 35.6$  kg m<sup>-3</sup> and the lowest density was of "Felina 32" granules  $-979.1 \pm 58.6$  kg m<sup>-3</sup>. The density of the pellets is high enough to meet the requirements for granulated biofuels.

Research results of investigated pellet strength (compressive strength) showed that at  $10.0 \pm 0.2\%$  moisture content of granules, the maximum critical force of compressive strength under pressure of "USO 31" granules were 742.5 N and the least resistant fibrous hemp "Finola" granules reached two times less force, 376.2 N.

The determined lower net calorific value of pellet dry fuel was very similar 17.37–17.44 MJ kg<sup>-1</sup>, which is close to the calorific value of many sorts herbaceous and energy plants.

After investigation of ash content formed by burning fibrous plant pellets, it was found that the lowest ash content is obtained from the incineration of "Finola" pellets -3.30%, and the highest -3.89 of "USO 31".

Melting characteristics of ash are important during combustion of biofuels, influencing chemical composition of ash the slag formation on the surfaces of burning implements. It is important for ash utilization and plant fertilization. By burning fibrous hemp pellets, their initial ash deformation temperature DT was very low and reached only 762–771°C. Burning of pellets produced from fibrous plants poses a risk of slag formation, but it is recommended to burn such pellets by mixing with wood waste pellets or pellets of plants which have a high ash melting temperature.

Due to the increasing interest in sustainable growth principles biomass ash needs to be suitably managed. The highest potassium (K), calcium (Ca) and phosphorus (P) concentration was found in the ash of "USO 31" (7986.2 mg kg<sup>-1</sup>, 7227.8 mg kg<sup>-1</sup> and 557.8 mg kg<sup>-1</sup>, respectively). When evaluating the amounts of heavy metals found in the ash of fibrous hemp pellets: copper (Cu), zinc (Zn), tin (Al), cadmium (Cd), it was found that they are not high and do not exceed the permissible values.

#### CONCLUSIONS

Fibrous hemp is suitable for granular biofuel preparation. Pressed fibrous hemp meet the quality characteristics and standard requirements for biofuel pellets. Burning of pellets from fibrous hemp poses a risk of slag formation, therefore it is recommended to burn such pellets by mixing with wood waste pellets or pellets of plants which have high ash melting temperature.

The chemical composition of ashes was dominated by the macroelements K, Ca, P, which suggests possibility for their agricultural use. The low content of heavy metals, such as Cu, Zn, Al and Cd should not be a limiting feature in their use.

Keywords: fibrous hemp, biomass, pellets, properties, combustion, ash characteristics.

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# BIOENERGY PRODUCTION THROUGH MONO AND CO-DIGESTION OF TOMATO RESIDUES

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#### EXTENDED ABSTRACT

#### **OVERVIEW**

The agro-industry of tomato generates 3 types of residues: ripe rotten tomato (unfit for consumption) (RT), green (unripe) tomato (GT), and tomato branches including leaves and stems (TB). These residues are commonly wasted or used as feed for livestock. Energy production through anaerobic digestion is an alternative way to manage and simultaneously valorise these materials. Thus, this work aims to optimize the operational conditions that maximize methane production and assess the anaerobic co-digestion of tomato residues.

#### **METHODS**

Rotten tomato (RT), green tomato (GT), and tomato plant (TB) were collected to be used in the anaerobic digestion. RT and GT were minced and dehydrated to reduce the moisture content by > 80%. TB was dried and then milled. The tomato residues were characterized in terms of total solids (TS), volatile solids (VS), pH, and lignin content according to standard methods. Designs of experiments were conducted to assess the effect of some of the most important anaerobic digestion conditions and the effect of different mixtures of all tomato residues (RT, GT, and TB) on anaerobic digestion performance. A 2-level fractional factorial design (25-1) was performed to evaluate the most relevant conditions affecting the biochemical methane potential (BMP). For his purpose, five factors with two levels were investigated: substrate to inoculum ratio (SIR), concentration of total volatile solids (VSt), working volume (WV), nutrients (Nu), and inoculum incubation (Inc). After obtaining the optimum operational conditions, an augmented simplex centroid design (ABCD design) was used to determine the mixture composition that maximizes the BMP. The anaerobic digestion assays were performed in sealed bottles of 1 L, using manometric measurements to obtain the BMP. The flasks were prepared with an inoculum of a wastewater treatment plant from the central region of Portugal and flushed with nitrogen to assure the absence of oxygen. The bottles were placed in an oven at 37 °C for 50 days and were shaken once a day. The incubation of the inoculum was carried out at 37 °C for 4 days before running the BMP assays. The nutrient solution was prepared as reported by Angelidaki et al. [1].

#### RESULTS

The tomato fruit residues (RT and GT) presented the lowest content of total solids (lower than 8%), while TB presented the highest content with 71%. As expected, the pH of tomato fruit residues ranged from 4.00 to 4.75 and the pH of TB was around neutrality (6.82). Regarding the lignin content, TB showed higher concentrations ( $20.27 \pm 0.44\%$ ) than RT and GT ( $7.87 \pm 0.29\%$  and  $4.11 \pm 0.85\%$ , respectively).

The 2-level fractional factorial design was performed with rotten tomato as reference. This design of experiments revealed that SIR is the most important factor affecting the BMP results. Indeed, two major groups were identified: i) one composed by the assays performed with SIR of 0.5, which achieved higher methane productions in a range of 86 to 310 NmL<sub>CH4</sub>/gvs, ii) and another composed by the tests carried out with SIR of 1.5, which attained lower methane yields (12-75 NmL<sub>CH4</sub>/gvs). The inhibitory effect observed for SIR of 1.5 is probably caused by a rapid accumulation of fermentation intermediates (such as VFA) [2-4]. VSt and some interactions have also revealed significant (p < 0.05) influence in the response variable (BMP). A predictive model with a root mean square error (RMSE) of 32.57

 $NmL_{CH4}/g_{VS}$  was developed with the significant factors indicated in Table 1. The optimum operational conditions were obtained maximizing the desirability function. A maximum of 296.7 ± 33.5  $NmL_{CH4}/g_{VS}$  is achieved when the operating conditions are set in the following levels: SIR = 0.5, VSt = 20 g/L, WV = 20%, in the presence of Nu, and the use of not incubated inoculum. The maximum predicted BMP was validated with experimental results.

Table 1. 2<sup>nd</sup> order factorial model for BMP (NmL<sub>CH4</sub>/g<sub>VS</sub>) prediction through the operational conditions of anaerobic digestion.

$\mathbf{BMP} = +480.554 - 278.423 \times \text{SIR} - 6.392 \times \text{VSt} + 3.477 \times \text{SIR} \times \text{VSt} + a1 \times (\text{VSt}-27.5)$						
$+ a2 \times (WV-30) + a3 \times (VSt-27.5) + a4$						
Coefficients						
(Nu,Inc)	a1	a2	a3	a4		
(Y,Y)	-1.726	-2.795	2.731	12.951		
(Y,N)	-1.726	-2.795	-2.731	-12.951		
(N,Y)	1.726	2.795	2.731	-12.951		
(N,N)	1.726	2.795	-2.731	12.951		

Y/N (Yes/No) corresponds to the presence/absence of nutrients or the addition/ not addition of incubated sludge.

Anaerobic co-digestion was assessed considering the optimum operational conditions reported before. The BMP results obtained from the mixture design are presented in Fig. 1. Reactional mixtures with more than 50% of RT or GT presented the highest methane productions. The BMP was maximum (373  $\pm$  7 NmL<sub>CH4</sub>/gvs) for a reactional mixture composed of 67% of RT, 17% of GT, and 17% of TB. No significant differences (p <0.05) were observed between the anaerobic digestion of RT and GT. Lower methane yields were observed for reactional mixtures with more than 50% of TB since it contains a higher amount of hardly biodegradable component (lignin). The BMP of 100% RT and 100% of TB are in agreement with the literature [5-10]. The special quartic model presented the best fit to the experimental results, so it was used to evaluate the anaerobic co-digestion. The model predicts the BMP with an RMSE of 35.80 NmL<sub>CH4</sub>/gvs and presents the significant factors that affect the response (Eq. 2).





$$BMP = 287.015 \times RT + 303.402 \times GT + 133.452 \times TB + 296.164 \times GT \times TB + +5437.321 \times (RT^2 \times GT \times TB) - 5458.165 \times (RT \times GT^2 \times TB)$$
(2)

The optimum mixture composition was obtained maximizing the desirability function. A maximum of  $324 \pm 38 \text{ NmL}_{CH4}/g_{VS}$  is achieved with a reactional mixture composed of 63% of RT, 20% of GT, and 17% of TB, corresponding to a synergetic co-digestion performance index of about 1.20.

#### CONCLUSIONS

In summary, the solid to liquid ratio and the concentration of total volatile solids are the main factors affecting anaerobic digestion process. The biochemical methane potential was maximum ( $297 \pm 34$  NmL<sub>CH4</sub>/g<sub>VS</sub>) for a substrate to inoculum ratio of 0.5, a total concentration of volatile solids of 20 g/L, working volume of 20%, in the presence of nutrients, and in the absence of incubated inoculum.

Regarding the anaerobic co-digestion, lower methane productions were obtained with a reactional mixture with more than 50% of the tomato plant. The anaerobic degradation of a mixture composed of 63% of rotten tomato, 20% green tomato, and 17% of tomato plant reached the maximum methane production ( $324 \pm 38 \text{ NmL}_{CH4}/g_{VS}$ ).

**Keywords**: Agro-industrial residues, Operational conditions, Co-digestion, Biochemical methane potential, Design of experiments.

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# A COMPARATIVE REVIEW OF BIODIESEL AS A RENEWABLE SOURCE FOR DIESEL ENGINE

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#### ABSTRACT

Today the major goal of environmental initiatives around the world is to prevent the destructive environmental pollutions. In particular, Directive 2008/50/EC «Ambient air quality and cleaner air for Europe».

As it turned out, one of the main consumers, which accounts for about 65% of world oil demand, is the transport sector. It is known, also, that the transport industry is directly related to the anthropogenic emissions of greenhouse gases that are the result of global warming and, as a result, the constant change of the Earth's climate.

In recent decades, industrial research has been successfully conducted around the world to study renewable fuels. Under current to many scientists, biodiesel deserve special attention. Production of biodiesel fuel is based on chemical processing of lipids of various bio resources.

According to most studies, during the combustion the biodiesel significantly reduced hydrocarbon content, solid, soot particles, carbon monoxide, and aromatic compounds compared to traditional diesel. At the present time, biodiesel can be more effective if used it as a complement to fossil fuel. The main task of the present study is to review of alternative fuels for CI engine. This paper will examine three major renewable feedstocks for refuelling diesel vehicles: animal fats, vegetable oils and waste cooking oils.

In conclusion, it can be noted that the production of such biodiesel will not only avoid competition with the sector for the fossil fuel industry, but also solve at least partially, the problems of waste disposal. Also, one of the key benefits of biodiesel is no need for modifications diesel engine.

Keywords: diesel engine, biodiesel, feedstocks, properties, emissions

## INTRODUCTION

Today in the automotive industry two types of engines are usually used [1]. They are diesel and gasoline engines. Over time, the diesel engines have progressed, developed and became more advanced than the gasoline engine. The market demand for diesel engine is increasing every day. The diesel engine, was named after the inventor Rudolf Diesel, is a common type of internal combustion engine [2]. It is a multi-cylinder piston engine. Internal combustion is used, which ignites as a result of an increase in temperature during air compression.

The compression ratio in a diesel engine is significantly higher than in a gasoline engine, since it is necessary for auto-ignition and also beneficial for efficiency, as a result, a higher degree of expansion allows more energy. The most decisive advantage of a diesel vehicle is cost-effectiveness. A diesel engine consumes significantly less fuel than a gasoline engine.

Diesel emits less carbon dioxide than gasoline engines. Modern compression ignition engines work on fuel, the chemical and physical properties of which, as well as engine design solutions, allow forming lower CO<sub>2</sub> emissions than spark ignition engines with the same power

[3]. This means that the fuel consumption is correspondingly lower too. The lower the fuel consumption, the lower the  $CO_2$  emissions. In addition, optimally low emissions of other highly toxic exhaust gases and particulate matter are maintained.

However, diesel cars also have disadvantages compared to gasoline-powered cars. For example, a diesel engine takes more time to reach operating temperature in winter.

The main problem of diesel engines is the high level of emissions of  $NO_x$  [4]. It's useful to note, higher oil prices can significantly decrease the cost advantage of biodiesel. In addition, biodiesel production has a lower impact on the environment throughout its life cycle. Furthermore researches have also shown that emissions of CO, unburned hydrocarbons and particular matter of diesel engines are reduced using the biodiesel fuels [5,7].

The advantages of biodiesel are that it does not require engine modifications [6] has lower emissions carbon monoxide, hydrocarbons, dust and sulfur content, caused by more lower carbon ration to hydrogen in biodiesel [7].

Different scientific researches have been proved that biodiesel fuel reduce in CO, HC, and soot formation, but almost always increases the  $NO_x$  emissions [8,9] compared to petroleum based diesel fuel. The main factor about biodiesel is that the absence of sulphur content, generates fewer amounts of hydrocarbon, carbon monoxide, particulate matter and smoke compared to commercial diesel [10].

As indicated in the literature, increase in biodiesel blend percentage to diesel reduces the carbon monoxide emission due to the presence of more oxygen content in the biodiesel [1, 10, 11, 12, 13].

The main goal of the present research is to explore the ecologically acceptable and sustainable biodiesel based on vegetables oil, waste cooking oil and animal fats. In this regard, engine performance, combustion characteristics and summary of emissions exhaust gases in compression ignition engine were compared. Therefore, in this paper biodiesel comparing with identical conditions of regular diesel fuel.

The study of the biofuel renewable sources can be useful for a wide side of researchers, industrialists, engineers and who are interested on biodiesel fuels as a promising alternative replacement for fossil fuels.

## DIFFERENT FEEDSTOCKS FOR BIODIESEL PRODUCTION

Biodiesel is an oxygenated fuel consisting of long chain mixture fatty acids derived from edible or non-edible vegetable oils, animal fats and waste cooking oil [14,15]. Usually biodiesel feedstock's include four main categories:

1. Edible vegetable oil: rapeseed, soybean, peanut, sunflower, palm and coconut oil [16,17].

2. Non-edible vegetable oil: jatropha, karanja, sea mango, algae and halophytes [18].

3. Waste cooking oil [19,20].

4. Animal fats: beef tallow, pork lard, chicken fat [21,22].

If possible, the raw material must match two basic requirements: low production costs and quality production standards. Thus, choosing the cheapest raw material is crucial to provide low production costs for biodiesel. Fig. 1 demonstrates the share of use biofuel in Europe. Fig. 2 shows the EU consumption of biodiesel fuel.



Fig. 1. Total EU 2019 consumption for transport by biofuel type [23]



Fig. 2. - EU consumption of renewable diesel [24]

At the present time, biodiesel fuels can be more effective if used it as a complement to fossil energy resources. This paper will examine three major renewable resources for refuelling vehicles: animal fats, vegetable oils and waste cooking oils.

## **OVERVIEW OF PERFORMANCE, COMBUSTION AND EMISSIONS**

## Animal fats

Nowadays, there are various researches that have been published focusing on the issues related to different types of animal fats that are used to produce biodiesel, such as: beef tallow, pork lard, and chicken fat [21,22].

Animal fats are readily available in the slaughtering industry, where they are well managed to control the product as well as the processing methods. In addition, animal fats have the advantage that they have a low content of free fatty acids (FFAs) and water.

The cost of animal fat is substantially lower than the cost of vegetable oil [15].

Also, a lot of scientists have found that harmful emissions such as carbon dioxide (CO<sub>2</sub>), particulate matter (PM) were reduced through the usage of animal fats for biodiesel production. Biodiesel based on animal fats has a high cetane number (>60) compared to biodiesel in vegetable oil (48 to 55). It is known that a higher cetane number reduces NO<sub>x</sub> while lowering the temperature during the early start of the combustion process [25].

Scientists [26] carried out experiments with mixing turkey fats (TRFB) with diesel fuel (DF) by 10%, 20% and 50% (v/v) blends for the production of fuel mixtures with the designations TRFB10, TRFB20 and TRFB50.

The impact of TRFB blends on combustion, performance characteristics and flue gas of a single-cylinder with direct-injection diesel engine was investigated with different engine loads and at 2000 rpm of constant engine speed.

The conducted research showed that the maximum heat release rate (HRR<sub>max</sub>) and maximum cylinder pressure ( $CP_{max}$ ) for all engine loads of TRFB mixtures were higher than the DF values due to the low cetane number of TRFB and the faster combustion of fuel in the chamber after a longer ignition delay. During the test [26], it was found that DF have a higher exhaust gas temperature compare with biodiesel due to the longer duration of DF combustion at high loads.

Since the calorific value of biodiesel is lower than the DF, it was found that the brake specific fuel consumption for TRFB mixing are higher than of the DF. Other researchers [27] have analysed the performance, combustion characteristics and exhaust gases of the same engine at four different loads under 1500 rpm. In accordingly to the results, brake specific fuel consumption (BSFC) was increased, due the lower calorific value of chicken fat biodiesel than that of diesel. It has been observed that increasing the percent of chicken fat in biodiesel mixtures causes lower emissions of carbon monoxide, hydrocarbons, but at the same time the increase of NO<sub>x</sub> levels due to the high level of oxygen in the biodiesel. It has also been found that the heat release rate (HRR) and cylinder pressure when biodiesel from chicken fat was used at all loads are very similar to diesel fuel. Another researcher [28] in the study used for the investigation diesel fuel (D100), biodiesel (B100) and three kind of blends, mainly B25 (D75B25), B50 (D50B50) and B75 (D25B75) in a diesel engine, the results showed that D100 releases higher rate of energy as expected compared to B100 and its blends.

However, the results showed that the blends burn more efficiently used with the blend B75 producing the best engine efficiency and reasonably low fuel consumption.

The emission data showed that the B100 and its blends produce less unburned hydrocarbon,  $CO_2$  and  $NO_x$  emission compared to D100. The better thermal and emission performance of the blends is most likely due to their balanced chemical composition. This work also indicates that blended fuels with higher ratio of biodiesel are recommended to use in CIEs to ensure efficient combustion.

Other authors [29] in experimental work, have established that BSFC decreases at higher load for all fuel types because the percentage increase in fuel required for engine operation is less than the percentage increase in power, which means that self-ignition engines operate more efficiently with full load torque than as part load. Also, it was observed increase emissions of  $NO_x$  while exhaust gas temperatures, CO emissions and hydrocarbons decrease with increasing amounts of biodiesel.

### Vegetable oils

The main advantage of vegetable oils such as palm, karanja or olive are their combustible property, allows us to consider these products as an alternative fuel [16,17,18]. Nowadays the most common between edible vegetable oils are soybean, rapeseed, sunflower, palm, coconut, olive, false fax, safflower, sesame, marula, pumpkin, African peer seed, Sclerocarya birrea, Terminalia catappa L., yellow nut-sedge tuber, rice bran. Inedible vegetable oils consist from castor, stillingia, tomato seed, zanthoxylum bungeanum, cottonseed, radish Ethiopian mustard, mahua, cuphea, ruberseed, treminalia, kusum, michelia, neem, see mango, eruca sativa gars, pilu, polanga, milkweed, field pennycress, crambe, syringe, karanja, paradise,

deccan hemp, camelina, jojoba, Jatropha, moringa, poon, koroch seed, garcinia indica, cardoon, linseed, putranjiva, tobacco, desert date, cuphea, camellia, champaca [14, 30].

In recent decades, the problem of so-called food in comparison to fuel has worsened. The use of edible oils has provoked much controversy in science. The main question is if it is advisable to use cooking oil for the production of biodiesel, while many countries are suffering from food shortages [18].

A literature review of using both edible and inedible vegetable oils in compression ignition engine has established that selection of non-edible vegetable oils as renewable source of energy is more perspective and efficient with compare to edible crops.

Firstly, for this goal is possible to use non-productive land for cultivation of edible crops, for example, in the Forest belt or in poor areas.

Main advantages of inedible vegetable oils are renewability, lower emissions of contaminants, minimizing the environmental consequences. In other side the disadvantage of inedible vegetable oils to compare with diesel fuel are higher viscosity, higher freezing point, slightly higher fuel consumption, more reactive to oxygen, it has higher cloud and pour points and higher percentage of nitrogen dioxide emission [31].

It has long been established that vegetable and animal fats, because they have high levels of fatty acids, have higher viscosity, but due to dilution with diesel fuel, viscosity decreases improve their engine performance.

It was found that when adding 20% of edible vegetable oil to diesel fuel, good results were achieved. It is also taken into account that when mixing two different fuels, no negative chemical processors occur [33].

In the paper the engine oil emission characteristics of palm oil with diesel fuel (DF) by 5%, 10%, 15% and 20% (v/v) proportion was investigated to obtain fuel and found only 20% together with diesel fuel give satisfactory results for such important engine performance as engine efficiency and exhaust temperature. So, they had experiment that with direct injection of heated palm oil, the maximum braking efficiency occurs with a high compression ratio and shows 14,6% better results than the diesel and they also investigated the engine's brake power where 20% of the fuel mixture was 6% higher than fossil fuel. But the average pressure at a high compression ratio was lower than that of a diesel engine, carbon dioxide emissions were higher than those of diesel fuel.

Some researcher [31] used in his investigation non-edible various vegetable oils in compression-ignition engines. Here are the conclusions he came to. The fuel properties of 7 inedible oils (Jatropha, Karanja, Mauha, Linseed, Rubber seed, Cottonseed, Neem) primarily depend on the climatic region and, accordingly, on the soil due to higher viscosity and density, as well as low cetane number. Inedible oils can cause a number of problems in the operation of a diesel engine.

A number of articles describe how it is possible to achieve a reduction in viscosity for diesel fuel if a mixture based on vegetable fats is used. The main method is to heat the biofuel before the start of the injection system for different sources, the temperature should not be below 70°C. Some researchers heated the fuel to 100°C and even 135°C. It was found that at 100°C most vegetable oils had a viscosity similar to diesel fuel. It was also established that preheating eliminates increased emissions such as CO,  $CH_x$  and the engine shows high performance [13].

Some researchers conducted an experiment with the replacement of diesel fuel on palm, soybean and jojoba curcas oils [33]. During the experiment direct injection of the engine load on 25%, 50%, 75%, 100% was involved. Analysis shows that most effected summary of emissions (SE) are reduced by 3.91% and 15.66% for soybean and jojoba curcas respectively. Meanwhile emission of NO<sub>x</sub> for these vegetable oils is higher for soybean (edible) by 21.79%, jojoba curcas (non-edible) by 23.0% to compare with diesel fuel.

In another publication rapeseed oil with the addition of a catalyst NaOCH<sub>3</sub> in proportions B5, B20, B40, B50, B80 and B100 have been studied [34]. Emissions of particulate matter and CO were lower than those of the diesel engine for all mixtures. NO<sub>x</sub> emission rose only for B80 and B100 blends.

At the other scientific study brake specific fuel consumption, torque power output and exhaust emissions of various types of fuels mixed with crude palm oil in ratios of B5, B10 and B15 to diesel fuel respectively, have been analysed [35].

During the experiment different engine speeds 800 rpm, 1200 rpm, 1600 rpm, 2000 rpm and 2400 rpm were involved. It has been established that torque of engine for various fuel blends B5, B10 and B15 was lower than diesel by 5.6%, 14%, and 17%, respectively Also, the reduction of torque for each blends was observed to compare with diesel fuel, it was mainly caused by the higher viscosity of the biodiesel mixtures.

Consequently, this led to the delay of combustion, as a result in drops in power for B5, B10 and B15. Brake specific fuel consumption (BSFC) values of different mixtures were higher compared to fossil fuel caused by lower calorific value of the biodiesel mixtures. Notably, that the suitable volume ratio for diesel engines was B5, because its performance and brake specific fuel consumption were as most appropriate as diesel fuel.

It was found, also, that for B5 the carbon monoxide (CO) and carbon dioxide (CO<sub>2</sub>) were decreased. It has been found from the available literature that the feedstock of biodiesel derived from vegetable oils alone represents 70-95% of the total production cost. Therefore, selecting the appropriate feedstock is a vital issue to ensure low production cost of biodiesel.

### Waste cooking oil

Today cooking oil is one of the most sought-after products produced throughout the world. Culinary oil is present everywhere, where food is fried in oil, starting from households, food processing industries, fast food shops and restaurants.

Disposal of such oil mainly occurs in the environment, which adversely affects soil and water resources due to harmful compounds present in such oil. When this type of waste is processed into fuel in the presence of toxic components in the raw materials is not so important for the production of biodiesel.

A number of researchers emphasize that the negative effects of using waste cooking oil may arise from the presence of water in the lipid feedstock and free fatty acids. Also, diesel fuel based on used waste cooking oil may cause excessive engine wear. It is also believed that at high temperatures fatty acids form salts with metals and this causes damage to the engine or tanks [36]. Still the widespread use of this type of raw material is an advantage for the production of biodiesel fuel. Also, the production of biodiesel using waste cooking oil is cheaper than diesel and takes less financial costs. Since waste cooking oil have a higher cetane number, it favourably affects the efficiency of the engine. There will not also be a problem with the accumulation of waste. Important is the fact that when using waste cooking oil engine modification is not required.

Another reason to use waste cooking oil is an initiative of a number of countries that recognized the use of food raw materials for biofuels neither humane nor qualitative way to solve ecological problem. Therefore, many studies have concluded that biodiesel should be produced from non-food raw materials. Analysing these data should also take into account the physical-chemical characteristics. One of the main problems is the high viscosity which affects the higher fuel consumption compared to diesel fuel. Today, the viscosity of the fuel can be reduced in two ways: preheating or mixing waste cooking oil with diesel fuel in different proportions [36].

In the first study [12], waste palm oil and rapeseed oil were used. The tests were carried out under different injection pressures for both types of fuel and various injection points were also determined from - 25 to 0 crank angle degree. It was found that carbon monoxide emissions and hydrocarbons for biodiesel decreased with increasing load. For diesel fuel the nitrogen oxide (NO<sub>x</sub>) emissions were lower than for biodiesel. It is known that the specific nitrogen oxide emission depends on such factors as an increase in the injection time, an increase in the combustion fractions and also depends on the high oxygen content in the biodiesel fuel.

Other authors [37] have studied the performance characteristics and exhaust emissions using of a single cylinder four stroke with various compression ratio. The authors investigated waste cooking oil methyl ester in proportion of 20%, 40%, 60% and 80% with diesel fuel respectively with a constant engine speed of 1500 rpm. Conclusions were made about that at various loads, the results showed improved performance for biodiesel blends. Namely, the brake specific fuel consumption, the thermal efficiency and also brake power were similar to diesel fuel performance.

Some researcher [38] used biofuel mixtures which were produced from waste cooking oil in ratio diesel engine of B5, B10, B20, and B30. The experiment was conducted in a single cylinder diesel engine. Scientists have investigated the performance and emission characteristics at fuel injection pressure 170-220 bars. During the test, dependence with increase torque and brake power with increasing fuel injection pressure up to 210 bar was observed. It was found decrease of smoke opacity, CO and HC for biodiesel blends. But nitrogen dioxide and carbon dioxide emissions for each of the mixtures were increased. Since the calorific value of biodiesel fuel is lower than that of diesel fuel, respectively brake specific fuel consumption for biodiesel blends was higher than diesel fuel.

Some other authors consider that higher viscosity compared to diesel is the major limitations of waste cooking oil for utilization as a fuel in diesel engines [39].

## CONCLUSIONS

Based on this review we have various range of available raw materials for the biodiesel production which is one of the most important factors in development of renewable energy sources. They may be considered for the partial replacement of fossil fuel.

One of the key benefits of biodiesel fuels is the reduction of pollutant emissions from diesel engine exhaust. Generally, the only exception is nitrogen oxides  $(NO_x)$ , which are involved in the formation of ozone and smog.

Also follows, that the maximum cylinder pressure  $(CP_{max})$  and the heat release rate  $(HRR_{max})$  of biodiesel mixtures were higher than the diesel fuel values for all engine loads due to the rapid combustion of the fuel in the combustion chamber.

Many researchers have noted in their works that the diesel fuel at high loads has a higher exhaust gas temperature to compare with biodiesel blends. The brake specific fuel consumption and the exhaust gas temperature of the engine increase in two cases with pure biodiesel and its blends.

The carbon monoxide and hydrocarbon emissions in compression ignition engine with biodiesel and its blends were lower compared with diesel fuel. It was established that biodiesel mixtures produce fuel with high oxygen content and notably improve combustion.

In conclusion, it can be noted that biodiesel can partially substitute as a blending component of diesel fuel as a solution of environmental problems.

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# INFLUENCE OF ANAEROBIC CO-DIGESTION OF POULTRY MANURE AND CHICKEN CARCASSES ON BIOGAS YIELD AND METHANE CONCENTRATION

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#### EXTENDED ABSTRACT

#### **OVERVIEW**

The poultry industry is a progressive and prospective sector in the Baltic region. Poultry manure (PM) looks like an excellent and abundant raw material for anaerobic co-digestion (AD) because of its organic solids content of more than 20%. However, a high concentration of ammonia and organic nitrogen makes this substrate problematic to digest and causes inhibition [1]. Chicken carcasses are an unavoidable source of biomaterial in chicken farms. This biomass could be co-digested with manure or another biomass [2]. The aim of the work was to investigate the possibilities of processing poultry manure and chicken carcasses into biogas. The following tasks were set:

1. To determine the parameters of the process of anaerobic processing of a mixture of poultry manure and chicken carcasses into biogas.

2. To determine the biogas yield and quality from a mixture of poultry manure and chicken carcasses.

### **RESEARCH OBJECT AND METHODOLOGY**

A mixture of litterless poultry manure and chicken carcasses was used for the research. The research was performed in four stages. In the first stage, diluted litterless poultry manure was used. Experiments were performed on a laboratory digester operated under a mesophilic temperature of  $37 \pm 1$  °C. The daily input of the reactor consisted of 240.7 g of water and 158.7 g of chicken manure. The water was used to dilute the poultry manure, as the undiluted dry matter concentration of the manure was 38%. In all cases, a hydraulic bioreactor load of about 30-34 kg/m<sup>3</sup> was maintained, which ensured efficient mixing of the substrate and even distribution of feedstock in the biogas reactor. Also, the additional use of water reduced the microorganisms inhibition by nitrogen compounds. Volatile solids (VS) were determined by samples ignition at 550 °C. The volumetric organic load of 3.0 - 4.5 kg VS/m<sup>3</sup>\*d was used for experiments. An organic load of 3.0 kg VS/m<sup>3</sup>\*d by adding 27.2 grams of milled chicken carcasses, and further increased to 4.0 and 4.5 kg VS/m<sup>3</sup>\*d by adding 54.4 and 81.6 grams of milled chicken carcasses, manure further increased to 4.0 and 4.5 kg VS/m<sup>3</sup>\*d by adding 54.4 and 81.6 grams of milled chicken carcasses, manure increases, respectively. Experimental research was performed in the biogas laboratory of Vytautas Magnus University, Academy of Agriculture. The laboratory biogas digester system was used for the research (Fig. 1).



**Fig. 1.** Scheme of the laboratory biogas digester. 1 - reactor, 2 - heating mat, 3 - mixer controller, 4 - reactor system controller, 5 - temperature sensor, 6 - Ritter gas volume meter, 7 - biogas storage tank, 8 - biogas analyser, 9 - data logger

The laboratory bioreactor system consists of a 15-liter glass vertical reactor 1 with biomass heating mat 2, an electric mixer 3, a biogas meter 6 and a biogas storage tank 7. The biogas reactor maintains a set temperature measured by temperature sensors and controls the temperature and operation of the reactor mixing system by a processes controller 3,4. The mixing cycle and temperature of the biogas reactor substrate are controlled automatically. The collected biogas was analysed with an Awite AwiFlex biogas analyser 8. The gas analyser can measure methane (CH<sub>4</sub>), carbon dioxide (CO<sub>2</sub>), hydrogen sulfide (H<sub>2</sub>S) and oxygen (O<sub>2</sub>) in the biogas. CH4 and H<sub>2</sub>S concentrations were measured during the studies. CH<sub>4</sub> measurement range 0 - 100%, accuracy  $\pm 3\%$ , resolution 0.1%; H<sub>2</sub>S measurement range 0 - 3000 ppm, accuracy  $\pm 3\%$ , resolution 1 ppm. Samples of the test material were weighed on electronic scales KERN EG4200-2NM, measuring range 0 - 4200 g, accuracy  $\pm 0.02$  g, resolution 0.01 g. The pH of the raw material and the digested substrate was determined during each loading with a pH-213 meter with a measuring range from 2.00 to 16.00, accuracy  $\pm 0.01$ , resolution 0.01.

### RESULTS

Results of 80 days experiments show that poultry manure itself yielded between 1.25 and 1.42 m<sup>3</sup> biogas from m<sup>3</sup> of reactor volume during laboratory trials at 3.0 kg VS/m<sup>3</sup>\*d volumetric organic load. The addition of chicken carcasses increased organic load from 3.5 kg VS/m<sup>3</sup>\*d up to 4.5 kg VS/m<sup>3</sup>\*d and enhanced volumetric biogas yield from 1.53 up to 1.83 m<sup>3</sup> biogas/m<sup>3</sup> reactor volume. The content of methane in the biogas ranged from 55,0 – 58,4 % at the volumetric organic load of 3.0 kg VS/m<sup>3</sup>\*d to 59.0 – 62.3% at the volumetric organic load of 4.0 kg VS/m<sup>3</sup>\*d. However, the concentration of hydrogen sulfide in the biogas varied from 1500 ppm at a volumetric organic load of 3.0 kg VS/m<sup>3</sup>\*d to 3600-3850 ppm at the volumetric organic load of 3.5-4.5 kg VS/m<sup>3</sup>\*d. It is recommended that producers of biogas plants should use additional biogas desulfurization equipment. The steady process of anaerobic digestion of a mixture of chicken carcasses and litterless poultry manure indicated pH of the substrate, which was evenly retained at pH 8.0±0.1 at all tested organic loads.

#### CONCLUSIONS

1. Mixing chicken carcasses with litterless poultry manure increased biogas yield and methane concentrations. The increase of the organic load from 3.5 kg VS/m<sup>3</sup>\*d up to 4.5 kg VS/m<sup>3</sup>\*d improved volumetric biogas yield from 1.53 up to 1.83 m<sup>3</sup> biogas/m<sup>3</sup> reactor volume.

2. The process of anaerobic digestion of a mixture of chicken carcasses and litterless poultry manure waste was stable, pH of substrate kept at pH 8.0±0.1 at all tested organic loads.

3. The concentration of methane in the biogas ranged from 55.0 - 58.4 % at the volumetric organic load of  $3.0 \text{ kg VS/m}^{3*}$ d to 59.0 - 62.3% at the volumetric organic load of  $4.0 \text{ kg VS/m}^{3*}$ d.

4. The hydrogen sulfide concentration in the biogas varied from 1500 ppm at a volumetric organic load of 3,0 kg VS/m<sup>3</sup>\*d to 3600-3850 ppm at the volumetric organic load of 3,5-4,5 kg VS/m<sup>3</sup>\*d.

Keywords: anaerobic co-digestion, poultry manure, chicken carcasses, organic load, biogas, methane.

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# RESEARCH ON THE USABILITY OF COAL NANOPARTICLES AS A NANO FUEL ADDITIVE TO BIODIESEL-DIESEL BLEND FOR DIESEL ENGINES

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### ABSTRACT

Metal nanoparticles result in a significant improvement in engine performance and exhaust emissions, but they are toxic and associated with many environmental and health risks. The coal nanoparticles are hydrocarbon-based, so their health risks are much lower than those of metallic-based nanoparticles. Therefore, coal nanoparticles could be more environmentally friendly additives due to their nature. This study aims to investigate the usability of coal nanoparticles as a fuel additive in a diesel engine by evaluating their effects on fuel properties, engine performance, emissions, and combustion characteristics. The coal nanoparticles were synthesized by the mechanical ball milling process performed in a bench-top, high-speed vibrating ball mill machine and several characterization tests were performed to study the morphology of the synthesized coal nanoparticles. The coal nanoparticles were added in B10 (90 vol.% diesel + 10 vol.% biodiesel) fuel in a mass fraction of 100, 200, and 300 ppm using a mechanical stirring and ultrasonication process. The analysis of physicochemical properties of fuels showed that the addition of coal nanoparticles to B10 increased viscosity, heating value, and flash point temperature, while cold filter plugging point temperature reduced. The engine tests were carried out at a constant speed of 1500 rpm and 17.5 compression ratio for low, medium, high and full engine load conditions. The addition of coal nanoparticles to B10 reduced carbon monoxide emission and nitrogen oxide emissions by 10-28% and 17-22%, however, hydrocarbon emission and soot emissions increased by 18-37% and 14-31%, respectively. Among the coal nanoparticles dispersed fuels, the concentration of 300 ppm coal nanoparticles presented the best engine performance. It reduced the brake specific fuel consumption by 2.37%, while increased the brake thermal efficiency by 2.06%, compared to B10. A slight reduction in-cylinder pressure and heat release rate for all nano fuel blends was observed.

Keywords: Nano fuel, Coal nanoparticle, Biodiesel, Diesel engine, Emissions

## **INTRODUCTION**

The use of fuel additives as a pre-processing emissions control technique and/or engine performance booster has been received great attention from the scientific community. This is mainly because there is no need for changes in engine design and structure [1]. Therefore, the use of fuel additives has emerged as the cheapest and easiest way to diminish exhaust emissions and enhance engine performance. In this field, various fuel additives such as oxygenated fuel additives, cetane improvers, water, and nano-additives have been exploited to enhance fuel combustion, reduces exhaust emissions, and improve engine performance. However, in recent years there is a growing interest in the use of nano-additives due to their unique properties like high thermal conductivity, high surface-area-to-volume ratio, catalytic activity, and oxygen content. These properties promote better fuel-air mixing and enhanced combustion, in turn, improve engine performance and decrease in emissions [2].

In this context, recently, plenty of researchers have been conducted using nano fuel additives to investigate the effect on fuel properties, engine performance, and exhaust emissions.

Kannan et al. [3] investigate the use of ferric chloride (FeCl<sub>3</sub>) as a metal-based fuel additive at a dosage of 20 µmol/L in a biodiesel-powered diesel engine. Their result showed that this fuel additive could bring significant improvement in engine performance and emissions. For example, it was determined that brake specific fuel consumption (BSFC) was reduced by 8.6% while brake thermal efficiency (BTE) increased by 6.3%. Apart from that, a decrease in soot, CO, and HC emissions by 6.9% 52.6%, and 26.6%, respectively observed when this fuel additive was used compared to neat biodiesel. Chen et al. [4] scrutinized a diesel engine running on various nanoparticle-diesel blends. Three types of nanoparticles: aluminum oxide, carbon nanotubes, and silicon oxide were added in a dosage of 25 ppm, 50 ppm, and 100 ppm with neat diesel fuel. The blended fuels were tested in a single-cylinder water-cooled diesel engine. Tests were performed under constant engine speed of 1800 rpm and various load ranges from 0% to 100 % by 25% increment. The tests' findings indicated that there is an increase in BTE up to 18.8% while a decrease in BSFC up to 19.8%. Silicon oxide-diesel blends showed better results than aluminum oxide-diesel blends regards to combustion pressure, brake specific fuel consumption, and carbon monoxide emissions. The same authors pointed out that aluminum oxide and silicon oxide exhibited stable blend conditions while carbon nanotube blends were the least stable. Wu et al. [5] investigated the effect of carbon-coated aluminum (Al@C) nanoparticle addition to diesel-biodiesel blend on engine performance and emissions. They concluded that when Al@C nanoparticles were added into the diesel-biodiesel fuel in the mass fraction of 30 ppm, a decrease in BSFC, CO, and NO<sub>X</sub> emission by 6%, 19%, and 6%, respectively could be achieved. However, despite these improvements, nanoparticles increased the soot number by 2.2 times on average. Also, they stated that after combustion Al@C nanoparticles have been turned into alumina nanoparticles. Manigandan et al. [6] investigated the effect of Zinc oxide (ZnO) and Titanium dioxide (TiO<sub>2</sub>) nanoparticle addition on dualfuelled diesel engine's performance and emissions. Zinc oxide and Titanium dioxide at a mass fraction of 50 and 100 ppm were blended with corn-vegetable oil methyl ester via ultrasonication. The study revealed that the addition of ZnO and TiO<sub>2</sub> nanoparticles to biodiesel improved BTE and BSFC while they reduced the values of CO, HC, NOx, and smoke opacity emission. It is stated that this was due to an improvement in the combustion rate owing to nanoparticles' large surface area and catalytic effect. Lastly, they reported that TiO<sub>2</sub> nanoparticles were superior to ZnO in terms of performance and emissions. Khatri et al. [7] studied the influences of silicon dioxide (SiO<sub>2</sub>) nanoparticles on the performance and emission characteristics of a water-diesel emulsified fuel-powered diesel engine at various injection timings. SiO<sub>2</sub> nanoparticles were added in four quantities as 25, 50, 75, and 100 ppm to waterdiesel emulsion fuel. From the experiments, it was concluded that the optimal nanoparticle dosage was found to be 50 ppm, which resulted in the lowest emissions and the best performance. Soudagar et al. [8] experimentally researched the performance and emissions features of a common rail direct injection diesel engine fueled with a diesel-biodiesel fuel blend (B20) and its blend with strontium-zinc oxide (Sr@ZnO) nanoparticles. The Sr@ZnO nanoparticles were blended with theB20 fuel in mass fractions of 30, 60, and 90 ppm using a magnetic stirrer and ultrasonication device. It was determined that the 60 ppm of Sr@ZnO nanoparticles showed overall enhancement in engine characteristics compared to B20 fuel. However, it was stated that the inclusion of nanoparticles in the B20 fuel increased the cost of fuel. Nevertheless, the authors said that the increase overall in engine performance could overcome the high fuel cost. Mardi et al. [9] in their study introduced three novel emulsion fuels

which consist of a large spectrum of additives such as nano-metal particles (Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>) and carbon nanotubes (CNT), cetane improvers, alcohols, water, and emulsifiers. The reasons for using multiple additives was to compensate for the disadvantages of each fuel. The experimental result clarified that the first fuel mixture which consists of CNT resulted in a significant increase in performance compared to diesel and biodiesel. The second fuel mixture that included  $Al_2O_3$  nano additive yielded the highest brake thermal efficiency. The third fuel mixture that included TiO<sub>2</sub> nanoparticles showed the lowest smoke opacity. But on the other hand, this mixture led to a decrease in BTE by 6.6%. As a conclusion, the authors said that emulsion fuels including different additives would provide clean alternatives for diesel. Recently, in the literature, graphene oxide nanoparticles [10,11], carbon nanotubes [12,13], quantum dots [1,14], and bio-nano additives [15,16] have received much attention from

researchers, as they are less toxic.

Khan et al. [10] investigated the effects of the use of graphene oxide nanoparticles on a common rail diesel engine's performance and emissions. The prepared and tested four nano fuel mixtures that included n-butanol, biodiesel, diesel by 30, 60, 90, and 120 ppm graphene oxide nanoparticles. The results showed that graphene oxide nanoparticles led to an improvement in engine performance, combustion characteristics, and emissions owing to their high catalytic activity. Moreover, it was inferred that graphene oxide nanoparticles could be more effective in reducing emissions and improving engine performance than their metal-based counterparts, due to their enhanced thermal and chemical properties.

As can be concluded from the above literature survey that metal-based nanoparticles possess a substantial improvement in engine performance and exhaust emissions [17]. But, metallic nanoparticles that release from the engine exhaust emit into the natural environment and this negatively affects living organisms due to their toxic nature [18]. Other important drawbacks of metallic nanoparticles are the high production cost and low product yield [19]. For these reasons, despite the effectiveness of metallic nanoparticles, their commercial use in engine applications does not exist today. Therefore, there is a need to develop high production yield, low-cost, non-toxic, and environmentally friendly nanoparticles that could be an alternative for metallic-based nanoparticles.

Coal nanoparticles (CNPs) could be alternative additives for metallic nanoparticles due to their low toxicity, environmental nature, low cost, high yield, and simple production methods. In the present study, to solve or alleviate the problems arising from the use of metalbased nanoparticles as a fuel additive, for the first time, the usability of the coal nanoparticles was investigated. For this purpose, at first, the CNPs were synthesized and then some characterization studies by various techniques were carried out. Following, the produced CNPs were added to B10 in a mass fraction of 100, 200, and 300 ppm, and some physical fuel properties were measured. To assess the impact of CNPs on the diesel engine's performance, emissions, and combustion characteristics, a single-cylinder diesel engine was exploited to perform engine tests.

## MATERIAL AND METHODS

For the synthesis of coal nanoparticles, the top-to-bottom nanoparticles synthesis method was chosen. In this method suitable sized materials are transformed into smaller fragments (powders) by breaking down into fine particles through various techniques such as mechanical milling, thermal/laser ablation, sputtering, and electro-explosion [20]. To reduce the milling time and also to obtain further fine coal nanoparticles, the ball milling process was performed in a wet environment wherein ethanol was employed. Coal pieces and ethanol at a mass ratio of 1:5 were filled into the stainless steel mill jar of the ball milling machine (*OptoSense, USA*) and coal pieces were milled for one and half hours with a rotating speed of 1200 rpm. The

grounded coal particles were dried in a laboratory oven at 60 °C for 12 hours and then were used as a fuel additive. After synthesizing the coal nanoparticles (CNPs) characterization studies were performed. Scanning electron microscopy (SEM, JEOL JSM-7001F, Thermo Fisher Scientific, USA) was used to study the morphology of the synthesized CNPs. The particle size distribution of the coal nanoparticles was determined by a particle size analyser (Mastersizer 3000, Malvern Panalytical, United Kingdom).

In the next step, the synthesized coal nanoparticles were added at the concentrations of 100, 200, and 300 ppm to B10 fuel (the diesel and biodiesel fuel blend containing 90 vol.% diesel fuel and 10 vol.% canola oil biodiesel) and dispersed in the fuel by applying mechanical and ultrasonication process. Regarding the label of the prepared fuels, the B10Cx abbreviation was used in which B10 stands for the base fuel, "C" represents coal nanoparticles, and x implies the CNPs concentration in ppm. For example, B10C100 denotes the base fuel (B10) contains 100 ppm CNPs. Some physicochemical fuel properties of the prepared test fuels were measured by following the related test methods. The engine tests and measurement of the fuel properties were performed soon after the nanofuels preparation to take advantage of their stable conditions.

The engine tests were conducted on a 4-stroke diesel engine coupled to Eddy current dynamometer. The engine was a single-cylinder, natural aspirated, water-cooled, direct injection diesel engine with a cylinder bore of 87.5 mm, a stroke of 110 mm, and a compression ratio of 17.5. Rated engine power is 3.5 kW at full engine load and 1500 rpm. Figure 1 illustrates the schematic representation of the experimental setup. BOSCH BEA 060 was used to measure the emissions of CO, HC, CO<sub>2</sub>, and NO. Soot emission was measured by BOSCH BEA 070 device.

The engine tests were performed at a constant speed of 1500 rpm at loads of 25, 50, 75, and 100% that corresponding to the percent of maximum engine torque output. Since the engine was operated at a constant speed, all fuels produced equivalent brake power at the same load. The six readings for performance and emissions were recorded to increase confidence in measurements and the mean values were used for comparison. The uncertainties analysis was performed by following the method proposed by Holman [21]. The uncertainty of the measured and calculated parameters was given in Table 1. Cylinder pressure vs. crank angle data was recorded for 100 consecutive cycles and the mean data set was processed in *ICEngineSoft V.9.0* software to obtain combustion characteristics.



Fig. 1. Experimental setup

Parameters	Measurement Range	Resolution	Uncertainty	
Brake torque	0-90 Nm	0.1 Nm	±0.5 %	
Engine speed	0-9999 rpm	1 rpm	±0.06 %	
Air flow rate	-	-	<±0.8 %	
Fuel flow rate	-	-	<±0.7 %	
Temperature	-	0.1 °C	1 °C	
Brake thermal efficiency	-	-	<±0.96 %	
Brake specific fuel consumption	-	-	<±0.81 %	
CO emission	0-10 % vol.	0.001 %	±0.1%	
NO emission	0-5000 ppm	1 ppm	± 5 ppm	
Soot emission, k	0-9.99	0.01	$\pm 0.1\%$	

Table 1. Uncertainties of the measured and calculated parameters

# **RESULTS AND DISCUSSION**

## Characterization of the synthesized CNPs

SEM analysis is a substantial method for the studies of the surface of materials as it offers significant information regarding the morphology and size of the materials [8]. The SEM image of CNPs illustrated in Fig. 2. It is seen from the SEM image that CNPs are uniformly distributed and the shape of CNPs is almost spherical (some CNPs' shape is platy). Also, the diameter of the CNPs is in nanoscale but differs in magnitude. This is due to the aggregation of CNPs. However, the ultrasonication process breaks the clustered CNPs into smaller particles, which slows the aggregation and settling, in turn, an increase in nano fuel stability. As the diameter of the CNPs is smaller than the diameter of the holes fuel injector nozzle, it does not cause any clogging through the fuel line and the injector nozzle.

Particle size analysis is a measurement of the particle size distribution of powder materials [22] and is usually expressed as volume percentages. The particle size distribution graph of CNPs is shown in Figure 3. It can be seen from the figure that CNPs present two size distribution regions. The first one is between 0.01-0.1  $\mu$ m which holds the highest volume density and the second one is between nearly 0.1-10  $\mu$ m which peaks nearly 1  $\mu$ m. It is thought that the second region formed due to agglomeration and clustering of CNPs. As above mentioned, the clustered CNPs can be easily dispersed in the fuel by ultrasonication technique as ultrasonication breaks intermolecular and interactions among particles [10]. Consequently from the particle size analysis, it can be inferred that most of the CNPs are in a diameter less than 100 nm.



Fig. 2. SEM image of CNPs



Fig. 3. The particle size distribution of CNPs

# Physicochemical properties of test fuels

The results of the measured physicochemical properties of the fuel samples using TS EN ISO and DIN test methods are presented in Table 2. Regarding the measurement results, it is observed that the addition of CNPs to B10 does not significantly affect the fuel properties except for kinematic viscosity. A marginal increase in kinematic viscosity is observed with CNPs addition. As the CNPs' concentration is increased kinematic viscosity is increased and the highest viscosity is measured for B10C300 fuel which has a 9.7 % higher viscosity value compared to B10. A similar observation for nanoparticles can be found in Refs. [10,23]. A small increase in density and calorific value while a slight decrease in CFPP is realized with CNPs inclusion in B10. Moreover, CNPs addition to B10 does not show a significant effect on distillation temperatures.

Properties	Test Method	B10	B10C100	B10C200	B10C300
Density, @15 °C (kg/m <sup>3</sup> )	TS EN ISO 12185	839.2	839.2	839.4	839.4
Kinematic viscosity, @40 °C (mm <sup>2</sup> /s)	DIN 53015	2.99	3.14	3.25	3.28
Calorific value (kJ/kg)	ASTM D 240	45016	45133	45070	45129

Table 2. Measured fuel pr	operties
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Cold filter plugging point (CFPP), (°C)	TS EN ISO 116	-4	-5	-5	-6
Cetane index	TS EN ISO 4264	54.7	54.8	54.7	54.7
Flash Point, (°C)	TS EN ISO 2719	64.0	65.0	66.0	66.0
Distillation temperature (°C)	TS EN ISO 3405				
	Initial boiling point	164.4	168.4	167.2	166.0
	10 vol.%	212.6	214.6	213.7	214.8
	50 vol.%	288.8	288.9	289.2	288.4
	90 vol.%	340.7	340.2	340.9	341.0
	95 vol.%	351.2	350.9	351.8	352.0
	Final boiling point	360.8	359.3	361.0	359.1

### **Performance Characteristics**

BSFC is the amount of consumed fuel to produce one kW power per hour. BSFC plot is shown in Figure 4a. BSFC values for test fuels decreased along with increasing load and the minimum BSFC values occurred at full load condition. This is due to the rising rate in brake power is higher than the growing fuel consumption. The results showed that the average BSFC values decreased at all CNPs concentrations compared to B10. But, although the sizeable difference in BSFC values was observed for 100 ppm and 200 ppm CNPs fractions the differences were within the BSFC uncertainty. On the other hand, the dosage of 300 ppm CNPs performed the best improvement in BSFC. According to the results, the average value of BSFC of B10C300 was decreased by 2.37% compared with B10. The main reason for the situation is due to the presence of CNPs which led to better air-fuel mixing thanks to the surface-area-to-volume ratio and high thermal conductivity. As a consequence of these effects, better combustion occurred and BSFC decreased. Besides, the high calorific value of nanofuels can provide higher combustion energy that reduces the BSFC.



Fig. 4. Variation of BSFC (a) and BTE (b) in different loads for test fuels

Figure 4b shows the variation of BTE values in different loads for test fuels. The result showed that the engine's BTE values increased at all CNPs concentrations. However, as observed in BSFC, the effect of 100 ppm and 200 ppm CNPs concentration on BTE was found insignificant since the increments in BTE were in the range of calculated BTE uncertainty. In the experiments, the test fuel which was prepared by adding 300 ppm CNPs to B10 presented the best improvement in BTE. An average increase in BTE was observed by 2.06% with the addition of 300 ppm CNPs in B10 compared to neat B10. This can be attributed to better mixture homogeneity through enlarging the contact area for air and fuel molecules which improve the combustion and thus BTE.

#### **Combustion Characteristics**

Figure 5a illustrates the variation of cylinder pressure (CP) vs. crank angle for test fuels at full engine load. The highest cylinder pressure was observed for B10 as 52.59 bar at 367 °CA (crank angle). This can be attributed to B10's low viscosity. The addition of CNPs to B10 slightly reduced the cylinder pressure. An increase in the mass fraction of CNPs is directly proportional to a drop cylinder pressure. This could be due to a decrease in the net heat release rate as seen in Figure 6. The maximum cylinder pressure for B10C100, B10C200, and B10C300 was recorded as 52.21 bar @367 °CA, 51.36 bar @ 368°CA, and 50.73 bar @369 °CA, respectively. Moreover, B10C200 and B10C300 retarded the peak cylinder pressure by 1 °CA and 2 °CA compared to B10.

Net heat release rate (NHRR) gives significant information about how fast the combustion process happens and where the combustion starts and terminates [24]. The variation of NHRR at full engine load for test fuels is shown in Figure 5b. It can be seen that the NHRR decreased by the addition of CNPs to B10. The same trend was also observed in CP. The peak NHRR decreased gradually with increasing the concentration of CNPs. This could be because the addition of CNPs to B10 led to an increase in viscosity and consequently decreased the NHRR. The maximum NHRR for B10, B10C100, B10C200, and B10C300 was calculated by 30.52 J/°CA@355 °CA, 28.07 J/°CA@356 °CA, 27.72 J/°CA@355 °CA, and 22.08 J/°CA@356 °CA, respectively.



Fig. 5. Variation of CP (a) and NHRR (b) at full engine load for test fuels

### **Emission Characteristics**

Figure 6a shows the variation of CO in different loads for test fuels. It is seen that the addition of CNPs in B10 reduced the CO emission at all investigated load conditions. The reduction in CO emission can be attributed to unique properties of CNPs such as high contact surface area, catalytic activity, and somewhat high energy content, which provides better mixing and oxidation. The average reduction in CO emission was determined by 20.02%, 11.34%, and 10.20% for B10C100, B10C200, and B10C300, respectively compared to B10. However, when the CNPs concentration is increased, the viscosity of the fuel blends raised, so a slight increase in CO emission was observed. Figure 6b demonstrates the variation of HC in different loads for test fuels. From the figure, it is observed that the formation of HC for all test fuels was drastically increasing with increases in engine load from 25% load to 75% engine load condition, and then decreased at full load. The high cylinder temperature at full load enhances the fuel oxidation and results in a low amount of HC emission. It was seen that the addition of CNPs to B10 increased HC emission. An average increase in HC emission by

28.93%, 18.58%, and 38.16% was observed for B10C100, B10C200, and B10C300 respectively compared to B10. The reason for this could be high fuel viscosity that deteriorates the fuel atomization and leads to incomplete combustion. The minimum mean HC emission was observed for 200 ppm CNPs concentration. Hence, the optimum CNPs dosage is 200 ppm in terms of HC emission.



Fig. 6. Variation of CO (a) HC (b) in different loads for test fuels

The variation of NO emission in different loads for test fuels is displayed in Figure 7a. It can be seen that NO emission got raised with the increase in engine load due to the higher combustion temperature. This increment can be explained by the fact that NO is mainly formed at high flame temperatures and particularly at high engine loads [8]. The inclusion of CNPs into B10 generated lower NO emissions than neat B10. The average reduction in NO emission for B10C100, B10C200, and B10C300 is 17.05%, 17.23%, and 22.49%, respectively compared to neat B10. This can be originated from the low heat release rate for CNPs blended fuels as seen in Figure 5b. A decrease in heat release rate could cause a temperature drop in the combustion chamber in turn a decrease in NO formation rate. Out of all test fuels, B10C300 has revealed the lowest NO emission. At the same time, it presented the lowest heat release rate. Therefore, these results are consistent with each other. Smoke emission from the diesel engine is emitted mainly due to oxygen deficiency at rich mixture zones, high fuel viscosity, and high carbon to hydrogen ratio of the fuel [9].

Figure 7b depicts the variation of soot emission (smoke opacity; smoke absorption coefficient) in different loads for test fuels. An increase in soot emission for all test fuels was found directly proportional to an increase in engine load. This is due to a decrease in the air-to-fuel ratio as the engine load is raised. As can be seen from the figure, the addition of CNPs to B10 increased the soot emission. The main reasons for the increment in soot emission for nanofuels could be the high viscosity and high carbon content. The addition of CNPs to B10 also increased the carbon content of the fuels, which creates further soot emission. Another possible reason for high soot formation could be attributed to the ash content of the CNPs. The average raise in smoke emission for B10C100, B10C200, and B10C300 was calculated as 14.29%, 31.26%, and 25.57%, respectively, compared to neat B10.



Fig.7. Variation of NO (a) soot emission (b) in different loads for test fuels

# CONCLUSION

In this study, the usability of coal nanoparticles as a nano fuel additive in a diesel engine by evaluation of its effects on fuel properties, engine performance, emissions, and combustion characteristics were researched. The results showed that CNPs could be synthesized by the ball milling method and the particle size of the synthesized CNPs was found smaller than 100 nm. The inclusion of CNPs into B10 increased the fuel viscosity by 5.0%-9.7%, also a slight rise in fuel's calorific value and flash point temperature was observed. The addition of 100 ppm and 200 ppm CNP to B10 increased the engine performance but the increments were found within the calculated uncertainties. The best engine performance was obtained for the 300 ppm CNPs concentration. It resulted in an average decrease in BSFC by 2.37% and an average increase in BTE by 2.06% compared to neat B10. The maximum CP and maximum NHRR decreased as the CNPs concentration increased. The addition of CNPs reduced the CO and NOx emissions but led to an increase in HC and soot emissions. The first findings of this study on the usability of CNPs as nano fuel additives showed that CNPs have the potential to be used in a diesel engine. However, the high soot emission emerged as a drawback. The soot emission could be reduced by improving the CNPs composition i.e. reducing ash and sulfur content.

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# UTILIZATION OF POULTRY BY-PRODUCTS BY ANAEROBIC CO-DIGESTION WITH COW SLURRY

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#### EXTENDED ABSTRACT

#### **OVERVIEW**

The poultry farming and processing industry's tremendous growth creates a large amount of offal and waste and encounters a challenge to utilize it. So far, burning technology was a popular and the easiest way to get rid of many organic by-products because it is cheap. On the other hand, burning technology contaminates the environment with carbon dioxide and nitrogen oxides. That problem drives us to determine whether anaerobic co-digestion of cow slurry with poultry by-product addition could be the environment-friendly technology that allows the utilization of poultry by-products. The latest studies show that cow manure could be co-digested with another biodegradable organic matter [1]. However, a high concentration of hydrogen sulfide obtained from protein-rich poultry waste makes research substrate problematic to digest with higher organic load and causes the hydrogen sulfide inhibition [2,3].

#### **METHODS**

The main task of the research was to determine the impact of chicken waste on the biogas yield and composition. The research has been conducted in the biogas laboratory of Vytautas Magnus University, Agriculture Academy on anaerobic co-digestion of cow slurry with chicken waste addition. The "Umwelt- und Ingenieurtechnik" BTP-2 laboratory biogas pilot reactor has been employed for that purpose and operated under the mesophilic temperature of  $37 + 1^{\circ}$ C. The laboratory bioreactor system consists of a 15-litre glass vertical reactor with electrical heating, an electric mixer, a biogas volume meter and a biogas storage tank. The mixing cycle and temperature of the biogas reactor substrate are controlled automatically. The collected biogas was analysed once a day with an AwiFlex biogas analyser. The gas analyser is equipped with methane (CH<sub>4</sub>), carbon dioxide (CO<sub>2</sub>), hydrogen sulfide (H<sub>2</sub>S) and oxygen (O<sub>2</sub>) cells. Samples of the test material were weighed on electronic scales KERN EG4200-2NM. The pH of the raw material and the digested substrate was determined during each loading with a Hanna PH213 meter. At first, an inoculum from a water treatment plant and cow slurry was used to start and inert the digestion process. The daily input of the reactor consisted of 720 g of cow slurry only. Cow slurry itself is highly diluted, and no water addition is needed. Dry matter varied at 7.3  $\pm$  0.2 % in all our experiments and allowed us to have the bioreactor's hydraulic load of about 52 kg/m<sup>3</sup>, ensuring efficient mixing of the substrate and good distribution of organic matter in the biogas reactor. In the further stages, the chicken waste was used to add to the reactor. The ratio of chicken waste to cow manure has been set as 3.77:100, 7.55:100 and 11.33:100 according to volumetric organic load 3.5 kg VS/(m<sup>3</sup>\*d), 4.0 kg VS/(m<sup>3</sup>\*d) and 4.5 kg VS/(m<sup>3</sup>\*d). A volumetric organic load of 3.0 kg VS/(m<sup>3</sup>\*d) was selected as a basis for further experiment. The organic load was increased to 3.5 kg VS/(m<sup>3</sup>\*d) by adding 27.2 grams of milled chicken waste, and further increased to 4.0 kg VS/(m<sup>3</sup>\*d) and 4,5 kg VS/(m<sup>3</sup>\*d) by adding 54.4 and 81.6 grams of milled chicken waste.

#### RESULTS

The Table 1 shows the influence of chicken waste addition to methane production (the biogas yield, methane concentration and methane yield).

Easting material description	Chicken	OLR, kg	Biogas	Methane	Methane
recuiling material description	waste, g	VS/m <sup>3</sup>	yield, l/kg	concentration, %	yield, l/kg
Cow slurry	-	3.0	15.9	60.2	9.6
Cow slurry + chicken waste 27,2	27.2	3.5	18.2	63.0	11.5
Cow slurry + chicken waste 54,4	54.4	4.0	21.4	66.9	14.3
Cow slurry + chicken waste 81,6	81.6	4.5	23.6	65.0	15.3

Table 1. Influence of chicken waste addition to biogas production.

The addition of chicken waste increased volumetric biogas yield on average 14.6%, 34.5% and 48.1% according to volumetric organic load of 3.5 kg VS/(m<sup>3</sup>\*d), 4.0 kg VS/(m<sup>3</sup>\*d) and 4.5 kg VS/(m<sup>3</sup>\*d). Methane concentration in biogas increased by 4.7%, 11.1% and 8.0% and methene yield – 16.4%, 42.2% and 53.1%, respectively. The addition of chicken waste material to cow manure substrate increased daily biogas yield and methane yield at all chicken waste and cow slurry ratios. Still, the highest increase of methane concentration was reached at volumetric organic load 3.5 kg VS/(m<sup>3</sup>\*d). The methane concentration in the biogas ranged from 60.2 to 63.0 % at the volumetric organic load of 3.5 kg VS/(m<sup>3</sup>\*d) and from 63.1 to 65.0% at the volumetric organic load of 4.0 kg VS/(m<sup>3</sup>\*d) and from 63.1 to 65.0% at the volumetric organic load of 3.0 kg VS/(m<sup>3</sup>\*d). At higher volumetric organic loads, after chicken waste addition, hydrogen sulfide increased significantly (to 4020 ppm) and to tackle the hydrogen sulfide inhibition problem, the addition of FeCl<sub>3</sub> was needed. The process of anaerobic co-digestion of cow slurry with poultry by-product addition indicated a steady pH value of the substrate over the entire experiments, which stayed at pH 8.0 on average at all tested organic loads.

### CONCLUSIONS

1. The research results showed that co-digestion of cow slurry with poultry by-product addition increased biogas yield, methane yield and the methane concentration in biogas at all volumetric organic loads.

2. The concentration of methane in the biogas was the highest and ranged from 63.1 - 66.9% at the volumetric organic load of  $4.0 \text{ kg VS/(m^{3*}d)}$ .

3. The hydrogen sulfide concentration has to be controlled constantly with the addition of desulfurization matter to avoid hydrogen sulfide inhibition throughout the entire process.

4. The biogas production process of anaerobic co-digestion of cow slurry with poultry by-product addition was stable enough with a slight deviation of pH value. The pH value of the substrate was around 8.0 at all organic loads.

**Keywords:** anaerobic co-digestion, methane concentration, biogas yield, cow slurry, poultry by-products, poultry waste, biogas.

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# BIOCHAR PHYSICAL AND MECHANICAL TREATMENT EFFECT ON THE SULFONATION EFFICIENCY

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#### ABSTRACT

Biochar is the solid product, which can be obtained in the thermochemical decomposition of biomass at temperatures higher than 350 °C under oxygen limiting conditions. Biochar can be used in different applications such as air separation and purification, vehicle exhaust emission control, solvent recovery because of its high specific pore surface area, adequate pore size distribution, and relatively high mechanical strength. Biochar can also be used as a catalyst and can be easily removed from the reaction mixture, washed, and activated again.

In this work birch chips were carbonized at 400 °C for 2 h and then used as a biochar in further experiments. Two methods have been tested to determine the effect on the sulfuric acid impregnation on the surface of biochar – physical treatment with water steam and mechanical treatment consisting of grinding and sieving to obtain different particle size fractions (<0.09, 0.2-0.4, 0.4-0.63 mm). For physical treatment different temperatures (850, 900, 910 °C) were used. Afterwards, for all obtained biochars sulfonation was performed. The functional group content to original biochar, mechanically, physically, and chemically treated biochars was determined via Boehm titration.

Results show that the functional group content is dependent on the particle size of the biochar and on the steam exposure temperature. For the grinded biochar, the largest total acidic group content was determined for sulfonated biochar with the particle size 0.4 - 0.63 mm, but the largest strongly acidic group content was for the biochar with the largest particle size without sulfonation. For the steam-exposed biochars the total acidic group content was approximately the same, but the largest strongly acidic group content was for the biochar that was steam-exposed at 850 °C and additionally sulfonated.

Keywords: biochar, lignocellulosic biomass, mechanical treatment, steam-exposure, sulfonation

## **INTRODUCTION**

Global challenges like the rapidly increasing consumption of fossil energy resources and the negative impact of these resources on the environment and public health promote the world to modify their strategies and shift from a fossil-fuel-based economy to a bio-resources-based one and the production of renewable biomass chemicals. Replacing fossil resources with renewable biomass resources is at the heart of the concept of a biorefinery [1]. Different processes exist that allow the transformation of raw biomass into desirable bio-based products and/or energy. For instance, biomass pyrolysis, which is a thermochemical process, transforms the raw material after heating in the absence of oxygen into bio-oil, gas and char [2]. The proportion of these three products depends on the pyrolysis conditions. Low temperatures (<600 °C) favour the production of bio-oil and biochar while high temperatures (>600 °C) maximize the production of gas. These pyrolysis products may be valorised in different applications. The bio-oil can be used as a fuel for heating, or for the production of chemicals [3]. Gas can be valorised into heat/electricity or further processed to produce biofuels. The solid bio-char can be gasified [4], used for the production of activated carbons [5], for the production of graphene [5], or for soil remediation [6].

Activated carbons are carbonaceous materials with highly developed internal surface area and porosity [7]. Activated carbon is widely used as an effective adsorbent in many applications
such as air separation and purification, vehicle exhaust emission control, solvent recovery, and catalyst support because of its high specific pore surface area, adequate pore size distribution, and relatively high mechanical strength [8]. It is important to note that activated carbon when used as a catalyst can be easily removed from the reaction mixture, washed, and activated again. In comparison sulfuric acid cannot be easily removed, recovered, or used several times.

The activation methods can be divided into two groups: physical activation and chemical activation. Physical activation is a process where the biochar materials are further exposed to a controlled flow of steam or  $CO_2$  or a mixture of them at temperatures above 700 °C. For chemical activation, the biochar is first impregnated in a solution containing different activation agents, followed by heating at elevated temperatures [9]. It is well known that in chemical and physical activation acid groups play a role in many types of catalytic reactions [10]. Acidic sites are formed on a char surface when oxygen reacts with defect sites on the surface, forming functional groups. Some of the functional compounds groups detected are carboxylic acids, lactones, or phenols (acidic) and pyrones or chromenes (basic) [11].

# METHODOLOGY

#### Materials and chemicals

Sulfuric acid (95 - 97 %), ethanol (96 %) were purchased from Merck and used without further purification.

#### Lignocellulosic biomass based char obtaining and activation

Figure 1 demonstrates the scheme for catalyst generation from lignocellulosic biomass. In further text the scheme is described more detail.

Ground birch chips (BC) (0.63 - 1.0 mm) were carbonized (Carb) at 400 °C for 2 h. There were two pathways for biochar treatment - mechanical and physical. First of all, mechanical treatment was done by grinding the carbonized birch chips and then sieving by different particle size sieves (<0.09, 0.2-0.4, 0.4-0.63 mm). The physical treatment was done with water steam at three different temperatures (850, 900, 910 °C) with constant water amount of 200 mL and flow rate 2.5 mL·min<sup>-1</sup>. After these treatments with all obtained biochars the chemical treatment was done by impregnating with concentrated sulfuric acid. Biochar was weighted (10 g) in a beaker and contacted with concentrated sulphuric acid (50 mL). Via periodic stirring (15 min) the concentrated sulphuric acid was mixed with carbon and placed in an oven at 80 °C overnight (20 h). After impregnation with sulphuric acid, the heterogenic biochar catalyst was suspended with 1 L deionized water and mixed for 30 minutes. Then the suspension was filtered, and the remaining heterogenic biochar catalyst was again suspended in 1 L deionized water and stirred for 30 minutes. This process was repeated in total 3 times. After that the heterogenic biochar catalyst on the filter was additionally washed with 1 L of hot deionized water (90 °C) until neutral pH was reached. In all rinsing steps the pH value of the water solution was measured with a Titralab TIM 840 automatic titration station. The heterogenic biochar catalyst was finally dried at 100 °C overnight (20 h).



Fig 1. Catalyst generation scheme

# Biochar catalysts functional group analysis with Boehm titration

To the mechanically, physically, and chemically treated biochars the functional group analysis was done by acid-base (Boehm) titration with Titralab TIM 840 automatic titration station. To approximately 0.5 g of heterogenic biochar catalyst, 50 mL of a 0.075 M NaOH or NaHCO<sub>3</sub> solution was added and left overnight at room temperature with constant mixing. The solution with biochar was then filtered and 5 mL of solution was back titrated with 0.1 M HCl until first stoichiometric point for NaOH and second stoichiometric point for NaHCO<sub>3</sub>. For each sample 3 replicates were done.

# Heterogenic biochar catalysts functional group analysis with FTIR

To qualitatively assess the formation of functional groups on the surface of the treated carbon, FTIR analysis (in ATR mode) was performed on the obtained biocarbon heterogenic catalysts. The heterogenic biochar catalysts were crushed to a fine powder and analysed directly. The FTIR data was collected using an attenuated total reflectance technique with a ZnSe and Diamond crystals on a Thermo Fisher Nicolet iS50 spectrometer. A total of 64 scans were averaged at 4 cm<sup>-1</sup> resolution for each spectrum.

# **RESULTS AND DISCUSSION**

In this work biochar was obtained via birch chip carbonisation and further the mechanical, physical, and chemical treatment were done. In physical treatment when oxidizing agent was used the biochar was exposed to either steam, ozone, carbon dioxide, or air at temperatures usually above 700 °C [12]. These oxidizing agents change the internal structure of the biochar, that results in opening and widening of inaccessible pores. Biochar activated in such environments have higher internal surface area and also abundance of oxygen functional groups that often works as active sites for adsorption [13]. Mechanical treatment by milling is a common method for increasing the surface area of the materials [14].

After each treatment on the biochar surface existing functional groups were analysed by acid-base titration and FTIR analysis. In the widely used titration method of Boehm, two bases of different strengths, NaHCO<sub>3</sub>, NaOH were used to neutralize oxygen functional groups of different acidities. NaHCO<sub>3</sub> neutralizes carboxylic acid functional groups and NaOH neutralizes carboxylic acids, lactones, and phenols [15]. For all biochars in the FTIR spectra the changes of the -SO<sub>3</sub>H group content was determined. In short, the -SO<sub>3</sub>H group changes corelated with the Boehm titration results, showing the same tendencies.

**Mechanically treated biochars: comparison between the original biochar.** After the acid-base titration results (Fig 2.) it can be seen that by comparing the original carbonized biochar with mechanically treated biochar the total acidic group and strongly acidic group content decreased for the biochar with particle size <0.09 mm but for the biochar with particle

size 0.2-0.4 mm the functional group content stays approximately constant, hence for the biochar with the largest particle size (0.4-0.63 mm) the functional group content increased. To explain these obtained results more experiments are needed.

**Mechanically treated biochars: comparison between different particle sizes.** With the increase of the particle size of the mechanically treated biochar, the total acidic and strongly acidic group content increases. This can be explained by fact that mechanical milling liberates non activated carbon material that has no active centres before or after impregnation. Since the number of functional groups is lower in small particle size fraction than in starting biochar it is possible that these non-activated charcoal parts are more concentrated in this small particle size fraction. None the less, to confirm this aspect further experiments are necessary.

**Mechanical and additional chemical treatment: comparison between mechanically and chemically treated biochars.** When the chemical treatment with concentrated sulfuric acid was done, the total acidic group content increases with the increase of the particle size, but the strongly acidic group content increases for the biochars with particle size <0.09 and 0.2-0.4 mm. For the biochar with particle size 0.4-0.63 mm the strongly acidic group content decreases.



Fig 2. Functional group content for mechanically and chemically treated biochars

**Steam-exposed biochars: comparison with the original biochar.** After Boehm titration results (Fig 3.) by comparing the original carbonized biochar with the steam-exposed biochars the total acidic group content decreased. This can be explained by the fact that the high-temperature steam activation causes a severe loss of the surface functional groups: phenolic and carboxylic [16–18]. In literature it is suggested that the functional groups on the biochar surface may have partially been degraded, as indicated by the decrease in the polarity index of biochar during the thermal activation using steam [17]. The strongly acidic group content for the steam-exposed biochars usually increases due to an increase in surface area and micropore volume [13].

**Steam-exposed biochars: comparison between steam temperatures.** By comparing the steam-exposed biochars at different temperatures the total acidic group content changes minimally with the increase of the temperature of water steam, but the strongly acidic group content slightly increases.

**Physical and additional chemical treatment: comparison between steam-exposed and chemically treated biochar.** After additional chemical treatment for these steam-exposed biochars the total acidic group content again changes minimally but the strongly acidic group content increased for the biochars with physical treatment at 850 and 900 °C, but for the biochar

with steam-exposure at 910 °C the strongly acidic group content decreased. The best strongly acidic group (-SO<sub>3</sub>H) content impregnation on the surface is achieved to the carbonized biochar at lower temperature (850 °C) of physical treatment. With the increase of temperature two factors are taking in place: firstly increased temperature promotes increase of the surface area of the heterogenic biochar catalyst, secondly increased temperature promotes degradation of existing functional groups already on the surface of the heterogenic biochar catalyst [19,20]. At temperatures above 800-850°C during activation with water steam, the small aromatic ring structures are gradually consumed; therefor, BC becomes more ordered so that less reactive structures are generated [21]. It should also be noted that O-containing groups at the beginning of the gasification process are gradually consumed as the carbon conversion increases, resulting in a decrease in reactivity [13]. With high temperatures overactivation can happen. In such situation, pores are developed, while walls begin to collapse, and pore sizes exceed the desired size for adsorption [13].



Fig 3. Functional group content for steam-exposed and chemically treated biochars

# CONCLUSIONS

In this work we tested the physical and mechanical treatment effect on the sulfuric group impregnation on the surface of the carbonised biochar. The functional group content to original biochar, steam-exposed and grinded biochars were determined by Boehm titration. The functional group content is dependent on the particle size of the biochar. Before sulfonation the largest total acidic and strongly acidic group content is determined for the biochar with particle size 0.4-0.63 mm. After sulfonation the total acidic group content is the largest for the biochar with the largest particle size (0.4-0.63 mm), but the strongly acidic group content – for the biochar with the smallest particle size (<0.09 mm).

The functional group content also depends on the steam exposure temperature. Before sulfonation the largest total acidic group content for all steam exposed biochars is approximately the same, but the largest strongly acidic group content is for the biochar that was treated with steam at 910 °C. After sulfonation the total acidic group content for all steam-exposed biochars also is the same, but the largest strongly acidic group content is for the biochar that was that was steam-exposed at 850 °C.

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# PLASMA ENHANCED CARBON CATHODES FOR BIOELECTROCHEMICAL REDUCTION OF CO<sub>2</sub>

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#### ABSTRACT

Although there are few methods to recycle, environmentally damaging CO<sub>2</sub>, the search still goes on for a method more efficient, more ecological and less energy consuming. An emerging technology is the bioelectrochemical system, which uses microorganisms as a helper in the process. Because it is a well interconnected system each component can play a role in the efficiency of it, the key is to improve those components that have the greatest impact.

In a bioelectrochemical system where reactions at the cathode are powered by electrons produced in anode compartment by microorganisms, the cathode material is very important in dispensing those electrons. A bad cathode material can have a double effect on the performance of the system. A weak flow of electrons from cathode surface leads to charge accumulation on the anode which in turn may diminish the proton flow between the two compartments. In this respect, the work at hand combines the recent developments in bioelectrochemical systems with the state-of-the-art electrocatalysts for  $CO_2$  electrochemical reduction. This study aims to highlight the role of cathode structure and morphology on the selectivity of a bioelectrochemical device. Surface chemistry was changed by an innovative plasma treatment that showed unexpected different (bio)electrochemical performances showing a decrease activity for treated electrodes. The work ends with a discussion on the role of bioelectrocathodes and strategies to mitigate losses leading to a higher performance.

Keywords: bioelectrochemical CO<sub>2</sub> reduction, products, cathode material.

# **INTRODUCTION**

Bioelectrochemical systems are an emerging technology which attract interest from many fields of study. Wastewater treatment and synthesis of chemicals have been targeted with bioelectrochemical systems. There are many other configurations that can be used in different domains [1],[2].

Usually, electrons and protons are generated at the anode which travel to the cathode via the external electrical circuit and the ion exchange membrane, respectively. Microbial fuel cells make use of the bio-generated electrons to generate power. The bioelectrochemical reduction of  $CO_2$  can be performed with electrons and protons, provided by the bioanode chamber, to recycle  $CO_2$  into other chemical products [1]. Electroactive bacteria such as *Shewanella oneidensis* can reduce electrodes by donating electrons as a by-product of their natural organic material oxidation process [3], [4]. These electrons can be rushed to the cathode with the help of a potentiostat were they meet with the protons that passed through a membrane from the anode chamber, together they help reduce  $CO_2$  in the presence of specialized  $CO_2$  reducing microorganisms such as methanogens or acetogens [5], [6].

In any bioelectrochemical system beside other factors (temperature, pH, circuit resistance), electrodes play a very important role in the performance of the system. Carbon materials shown

to be good and biocompatible as electrodes interacting with bacteria being easily reduced. Different forms of carbon such as: granules, graphite and other fiber material can be used to collect electrons from bacteria [2].

Beside a good anode, in a well performing system there is a need for a suitable performing cathode as well which can keep a constant flow of electrons in the medium which it reduces [7]. A poor performance of the cathode surface in delivering charges in the reduction reactions that take place, can affect the performance of products production. Studies show increase in performances for different treatments of carbon cathodes [9],[10] and other paper suggest increased electroactivity and bacterial attachment when plasma treated anodes are used [11],[12].

The aim of this study is to investigate the electrical performance of a carbon felt electrode, as cathode, that was treated in two different ways in plasma to modify the surface of interaction. Therefore, two modified electrodes were created, and their performance was compared with the results from an untreated one. These electrodes were used as cathodes in a bioelectrochemical system where the electron source, in the anode chamber, was a culture of *Shewanella oneidensis* grown on a rich medium. Chronoamperometry was performed by applying different potentials between the anode and cathode, measuring the current between. Data was linked with Raman spectrum for each electrode to better understand how surface can affect the electrode behaviour. Studying the performance of electrodes is a first key step in choosing the right one for future efficient CO<sub>2</sub> recycling system.

# MATERIALS AND METHODES

# **Electrode preparation**

Carbon felt (both from RHY, China) was used as electrode material for anode as well as for the cathode. Three carbon felt electrodes were tested as cathodes, two of which were pre-treated one hour in the ambient of induced plasma modifying one of their surfaces (approx. 2.5x2.5 cm<sup>2</sup>). Gas tank nitrogen and ambient air at 100 mL/min flow rate were used as working gas for the plasma discharge (approx. 250W) in a quartz tube using a radio frequency (2.46 MHz) in-



Fig. 1. Schematic representation of electrode treatment.

house build system. After plasma treatment the electrodes were analysed with Jasco NRS-3100 Raman spectrometer using the 523 nm laser beam. The experimental protocol is presented in Fig.1.

# **Bioelectrochemical system setup**

The system used was a 100mL bicameral configuration, autoclaved at 100° C for an hour. The anode chamber was filled with 90 mL of Luria-Bertani (LB) medium containing: tryptone 10g/L, NaCl 10g/L, yeast extract 5g/L and was put under continuous stirring. The medium was inoculated with Shewanella oneidensis MR-1 (LMG 19005) bacteria culture pre-grown one day before. The cathode chamber was filled with 90 mL phosphate-buffered saline (PBS) solution. The two compartments were separated by proton exchange membrane (Fig.2).

All the cathode electrodes were tested in the same day in the same system having an anode chamber redox potential of approx. -490mV vs sat. calomel before starting the chronoamperometry and between electrode changes. The system was connected to a VoltaLab PGZ 301 potentiostat having the cathode as the working electrode, the reference calomel electrode beside auxiliar electrode (anode) in the anode chamber. Chronoamperometry measurements were taken at potentials ranging from -500mV to -1500mV at 100mV step, each at 2 min. duration and with 5 min. intervals between measurements.



POTENTIOSTAT

CATHODE

**REFERENCE ELECTRODE** 

Fig. 2. Experimental setup

# **RESULTS AND DISCUSIONS**

Figure 3 shows Raman spectra of three carbon felt (CF) electrodes used in this experiment: untreated, air plasma treated and N2 plasma treated. Each graph after baseline subtraction contains two important carbon specific features (peaks) which were deconvoluted with Gauss-Lorentz functions.

G peak, which appears at around 1560 cm<sup>-1</sup> gives us information about the level of order in the surface arrangement at atomic levels of the materials. This information is showed in the intensity of the light reflected at 6410 nm. D peak appears at around 1350-1360 cm<sup>-1</sup> when the studied surface has defects and the deformed structural matrix bends the light, emitting in the 7353-7407nm range. The I<sub>D</sub>/I<sub>G</sub> intensity ratio, presented in Table 1, gives us information about the level of disorder in the material [8]. Knowing that we can say that the greatest disorder (4.04) is created in the air plasma treated electrode in comparison with the other two electrodes which seem to have similar ratios (1.96-untreated) and (2.11-  $N_2$  treated), this can be seen also from the change in the intensity of the peaks in all three graphs.

CF electrode	G area 1560 cm <sup>-1</sup>	D area 1350-1360 cm <sup>-1</sup>	Id/Ig
untreated	8.48E+06	1.66E+07	1.96
N <sub>2</sub> treated	4.16E+06	8.78E+06	2.11
Air treated	3.99E+06	1.61E+07	4.04

Table 1. Raman spectra data.



Fig. 3. Raman spectra of carbon felt electrodes: a) untreated; b) treated in  $N_2$  plasma; c) treated in air plasma.



Fig. 4. Carbon felt electrodes chronoamperometry investigation.

Fig. 4 shows results of chronoamperometry investigation for three carbon felt electrodes: air plasma treated,  $N_2$  plasma treated and untreated. Each point represents the current limitation average value for a set potential hold, between reference and working electrode, for each of the treated respectively untreated electrodes.

For all three electrodes, the potential difference was kept 2 min. at same values with a maximum difference of 1500 mV and a minimum difference of 500 mV with a step of 100 mV. The average current values were calculated for the second minute at each potential difference values.

The graph presents similarities for the treated electrodes with a minimum transport-limited current of -0.42mA (air treated), -0.52mA (N<sub>2</sub> treated) at -800mV potential and a maximum current of 2.1mA for both at -1500mV. The untreated electrode although has small current values in the beginning -0.6mA at -500mV it differentiates itself, from the others, reaching current values of 3.9mA at a potential of -1500mV.

These results seem show that the untreated electrode has a better conductivity surface then the other plasma treated electrodes.

Though we expected to improve the performance of the electrodes by plasma treatment, but the data indicates contrary to that, this may be due to grown resistance of the surface of the treated electrodes. Another possibility is that in the treatment process, when vacuum is created in the plasma chamber, oxygen, which otherwise is locked between the fibers, escapes creating a less reactive medium between the fibers in comparison with the untreated electrode.

#### CONCLUSIONS

The goal of this research was to study the improvement of electrode surface performance by plasma treatment, for further use of these electrodes in  $CO_2$  reduction. Although Raman spectra shows the change in the material surface morphology, chronoamperometry results indicate that none of the treatments applied in our study can improve the performance of our carbon felt electrodes.

The results show that both treated electrodes have similar performance which is much lower than that of the untreated electrode. This indicates that the untreated electrode can be more suited for our aim.

The thread like composition of carbon felt makes it hard to understand the effects of plasma treatment but the chronoamperometry tests suggest that the untreated carbon felt electrode can be more electroactive. Because of the complex nature of the carbon felt structure this subject needs further investigation to understand electrode behaviour after treatment. Furthermore, other electrode materials can be tested.

Finding the right electrode that can be used to help reduce  $CO_2$  and be biocompatible can accelerate the race to become carbon neutral and even carbon negative.

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# HYDROTHERMAL IN-SITU GASIFICATION OF METAL IMPREGNATED BANANA PSEUDO STEM FOR H<sub>2</sub> RICH GAS MIXTURE AND NANOMETAL CARBON HYBRIDS

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#### ABSTRACT

The major challenges like high ash, moisture content, and catalyst deactivation in the conventional thermochemical treatments (pyrolysis and gasification) can be overcome with the novel catalytic in-situ hydrothermal gasification. The banana pseudostem was initially impregnated with equal concentrations of the aqueous streams of Nickel and Ruthenium salts. During the impregnation, the alkalis and alkaline earth metals get replaced with metals that would eventually reduce the slag and salt precipitation. The metals loading was found to be 3.12 and 3.69 wt% for Nickel and Ruthenium, respectively. These Nickel and Ruthenium loaded banana pseudostem was then subjected to hydrothermal gasification over the temperature range of 300 - 600 °C with biomass to water ratio of 1:10 for 60 min residence time. The gas yields are proportional to the temperature, and the highest yields were 26.61 mmol/g with a carbon gasification efficiency of 76.65%. During in-situ hydrothermal gasification, the impregnated metals in M(<sup>n+</sup>) forms get transformed into M<sup>(0)</sup>. XRD in combination with TEM results confirms the carbothermal reduction towards the nanometal hybrids. These transformed nanometals (Ni && Ru) with advanced activity towards the breakage of C-C bonds promote the degradation of biomass into fuel gases. A maximum H<sub>2</sub> yield of 12.27 mmol/g was achieved at a maximum temperature of 600 °C with nanometal carbon hybrids of average particle size of 15 nm.

**Keywords**: Impregnation, hydrothermal, Nickel and Ruthenium, carbothermal reduction, nanometal hybrids.

### INTRODUCTION

Biomass is abundantly available and has been acknowledged as an environmentally friendly, sustainable, and renewable energy source for future generations. So far, the limited availability of fossil fuels has created the energy demand gap for the fast-growing population and industrial purposes. The over dependency and irregular consumption of fossil fuels have significantly affected our environment due to greenhouse gas emissions. In such scenarios, biomass and biowastes can be considered alternative renewable energy sources due to their abundant availability at meager cost and sustainability for waste management, economics, ecology, energy, and society [1]. Further, the generation of fuel from a high lignocellulosic compound containing biomass has gained much attention towards fulfilling the energy demand gap and can be used as a potential feedstock for the production of fertilizers, biofuels, biochar, ethanol, natural gas, methane, xylitol, and biogas. But, in recent year, the utilization of biomass have been more focused towards the generation of biochar via most economical and efficient conversion technique [2]

The assistance of long-term carbon sequestration is well managed with biochar obtained from the conversion of biomass. The biochar generated from biomass also enhances carbon stability and helps in  $CO_2$  capture and its utilization [3]. Therefore, it shows that biomass conversion into energy and biochar can be considered the most profitable, economic, and readily available

resources that can be used as a renewable, sustainable, and green technology in more versatile ways.

Biochar is a low-cost carbon-rich, stable, and solid porous material that finds several applications in wastewater treatment, bioenergy production, catalytic activities, environment remediation, soil conditioning, carbon sequestration, and agriculture-related activities [4–6]. Further, to enhance the properties and adsorption capability of biochar, various modifications have been reported by altering the surface charge of biochar with the incorporation of metal nanoparticles [7]. These nanometals ( $M^{(0)}$  and  $M^{(+n)}$ ) enhances the specific surface area, surface activities, and adsorption sites. However, ex-situ incorporation of nanometals into biochar can be energy-consuming and uneconomical.

Therefore, in this article, we proposed a novel method that can simultaneously generate energy in the form of hydrogen-rich syn-gas and highly dispersed metal nanometals  $((M^{(0)}/M^{(+n)}))$  into hydrothermally activated char (HAC). In this regard, banana pseudostem (Musa acuminate), which contains high lignocellulosic components (approx. 70 wt.%), was selected as it is abundantly cultivated in subtropical and tropical countries. Also, banana farming generates about 88% (by wt.) of agriculture residue in leaf and trunk [8]. According to the Food and Agriculture Organization (FAO) of the United Nations, the global production of bananas was estimated to be 116 million tonnes, and India alone accounting for 30.5 million tonnes in 2019 [9]. The metals (Ni and Ru) were directly impregnated into banana pseudostem. Later, this impregnated biomass was subjected to hydrothermal gasification at sub- and supercritical water (SCW) conditions to produce H<sub>2</sub>-rich syn-gas. This process simultaneously generates HAC embedded with nanometals ( $(M^{(0)}/M^{(+n)})$ . Apart from the biochar application mentioned earlier, the HAC generated in this process may also find its application as a raw material for energy storage devices, electrodes, supercapacitors, etc.

#### MATERIAL AND METHOD

#### Materials

The metal salts of Nickel [Ni(NO<sub>3</sub>)<sub>2</sub>· $6H_2O$ ] and Ruthenium [RuCl<sub>3</sub>· $xH_2O$ ] were purchased from Sigma Aldrich, India. The biomass (banana pseudostem) was collected from banana farming, Roorkee, India.



Banana Tree

Fig. 1. Banana pseudostem sample processing.

#### Methods

The biomass was cleaned and crushed using a knife mill to reduce the biomass size to less than 1 mm. The biomass was mixed with 0.05 M of each metal salt with a biomass to water ratio of 1:10 for 48 hours to maximize the uptake of the metals from the liquid effluent. Metals (Ni and Ru) were impregnated into biomass at zero point charge (pH<sub>ZPC</sub>), which was determined by the pH-drift method [10]. The slurry was then filtered off to obtained metal impregnated banana pseudostem that was further dried for characterization.

#### Supercritical water gasification

The metal impregnated biomass was then subjected to the sub- and supercritical water gasification in a 25 mL batch reactor (Inconel) set up. The setup comprises various high-pressure valves, tubings, Inconel reactor, gas-liquid separator, micro-filter, moisture trap, flow meter, and gas chromatography. The details of the experimental setup can be found elsewhere [9,10].

The reactor and the associated lines were primarily purged with inert N2 gas to make it oxygen-free. A known quantity of the biomass the water with a fixed ratio was fed into the Inconel reactor. The reactor was closed with the reactor cap and then set inside the split thermal furnace. The temperature was raised to the desired operating temperature, and the reactants were allowed to degrade into product gases. The outlet valve of the reactor was opened for the products to get separated into liquid and gaseous products. The product gas mixture was then passed through the moisture trap. The obtained dry gas was measured with a total gas flow meter and then directed to a gas chromatograph to quantify the individual gas components.

### Characterization

Raw biomass, metal impregnated biomass, and the hydrothermally treated char was characterized using various techniques like inductively coupled plasma mass spectrometry (ICP-MS with PerkinElmer, Model ELAN DRC-e), X-ray diffraction (XRD: BRUKER X-ray diffractometer (model D8 advance) operating at 40 kV and 30 mA using Cu K $\alpha$  radiation source ( $\lambda = 1.5406$  Å)), SEM–EDX (scanning electron microscopy–energy dispersive X-ray spectroscopy: FE-SEM QUANTA 200 FEG), and TEM (transmission electron microscopy; model JEOL-JEM-3200FS). The product gas mixture was analysed using a gas chromatograph (microprocessor-based gas chromatography system with model 5800). The TOC of the product liquid sample was quantified using a TOC analyser purchased from Shimadzu, Japan.

# **RESULTS AND DISCUSSION**

#### Characterization of raw, impregnated, and hydrothermal char

Chemical properties such as proximate, elemental analysis, and metals dispersion into metals- impregnated (BS-Ni-Ru) biomass and biochar samples were performed and compared with the raw sample (BS-Raw). These properties were illustrated in Table 1. The moisture content of raw banana pseudostem was evaluated to be 42.15 wt.%. The proximate analysis of BS-Raw resulted in the higher volatile matter (74.85 wt.%) with fixed carbon 15.07 wt. % and ash content 10.08 wt.%, making it a suitable renewable energy source. As compared to the raw sample, the BS-Ni-Ru samples show a slight deviation after metal impregnation. The volatile matter and fixed carbon decreased to 70.51 and 14.12 wt.%, whereas ash content increased to 15.37 wt. %. The ultimate analysis also demonstrates the decrement in the carbon and hydrogen contents in BS-Ni-Ru (C- 26.69 wt. %, H- 3.7 wt. %) compared to the BS-Raw sample (C-40.76 wt. %, H- 5.42 wt. %). The decrease in the volatile matter, fixed carbon, and carbon, along with the increase in ash content, can be attributed to the dissolution of water-soluble extractives and incorporation of metals (Ni and Ru) into biomass as metals have relatively higher atomic mass. The biochar generated after the hydrothermal treatment (temp.- 600 °C, B: W- 1:10, and R.T- 60 min.) shows the considerable loss in the volatile matter, whereas ash content and fixed carbon increased to 54.73 and 40.86 wt. %, which demonstrates almost complete valorization of biomass components. Similar results were reflected in the ultimate analysis of biochar.

Analysis	BS-Raw	BS-Ni-Ru	Char-Ni-Ru			
Moisture (wt. %)	42.15					
Proximate analysis (dry basis, wt. %)						
Volatile Matter	74.85	70.51	4.41			
			54.73			
Ash content	10.08	15.37	(magnetic			
			hybrids)			
Fixed carbon	15.07	14.12	40.86			
Ultimate analysis (dry and ash-free, wt. %)						
C	40.76	26.69	38.15			
Н	5.42	3.70	0.07			
Ν	1.24	2.92	0.22			
Ο	52.58	59.88	39.83			
O = 100 - (C + H + N + metal)						
Metal loading (wt. %)						
Ni		3.12	10.26			
Ru		3.69	11.47			

 Table 1. Chemical properties and metal loading analysis of raw, impregnate, and biochar of banana pseudostem samples.

The Ni and Ru metals were impregnated at the zero-point charge  $(pH_{ZPC})$  of biomass and metals salts aqueous solution  $(pH_{ZPC}-5.6)$ , which was determined by the pH-drift method. The amount of Ni and Ru loading was evaluated by ICP-MS analysis. The loading of Ni and Ru metals was 3.12 and 3.69 wt. % into the impregnated samples, whereas Ni and Ru were found to be 10.26 and 11.47 wt. % respectively in the biochar sample. Brewer et al. [11] and our previous work [8,10] demonstrate similar results.



Fig. 2. FE-SEM images of (a) BS-Raw, (b) BS-Ni-Ru, (c) Char-Ni-Ru, and EDX analysis of (d) BS-Raw, (e) BS-Ni-Ru, (f) Char-Ni-Ru, respectively.

The FE-SEM and TEM analysis determined morphological changes, elements determination, and particle size of dispersed metals. FE-SEM images reflect the distortion of the surface after incorporating metals into biomass (Fig. 2b) compared to the raw sample (Fig. 2a). Further, the FE-SEM image of biochar (Fig. 2c) reflects a more porous surface with more nanosize metal particles. The increased porosity after hydrothermal treatment in biochar

samples can also be seen in the SEM image (Fig. 2) of the samples compared to raw and impregnated biomass. The EDX analysis of BS-Raw, BS-Ni-Ru, and Biochar samples illustrated in Fig. 2, compliments the ultimate and ICP-MS analysis.

The TEM images of Ni and Ru dispersed biomass and biochar samples were shown in Fig. 3. The black spot represents the metal nanoparticles. The average size Ni and Ru of metal nanoparticles  $(M^{+n})$  was found to be 50 nm. The oxides/hydroxides form of nanometals present in the impregnated biomass were further reduced to their elemental state  $(M^{(0)})$  after the hydrothermal treatment of the samples (Fig. 3b and Fig. 4). The average size of the nanoparticles was evaluated to be around 15 nm.



Fig. 3. TEM analysis of (a) BS-Ni-Ru, and (b) Char-Ni-Ru



Fig. 4. XRD spectral analysis of BS-Ni-Ru, and Char-Ni-Ru samples

The XRD spectra of metals (Ni and Ru) impregnated biomass and biochar generated after gasification at supercritical water condition (Temp- 600 °C, Press- 25 MPa) was illustrated in Fig. 4. The spectral result of BS-Ni-Ru demonstrate the presence of Ni in the molecular form of Ni(OH)<sub>2</sub> ( $2\theta$ = 19.43), Ni<sub>2</sub>O<sub>3</sub>H ( $2\theta$ = 30.93, 37.96, 47.97, 49.39, and 58.8), and Ni<sup>(0)</sup> ( $2\theta$ = 44.18, and 77.6), corresponding to the JCPDS file No. of 00-003-0177, 00-040-1179 and 00-004-0850 respectively. Similarly, Ru impregnated into the biomass sample was reduced in the form of RuO<sub>2</sub> ( $2\theta$ = 27.8) and Ru<sup>(0)</sup> ( $2\theta$ = 37.96, 44.18, 58.8, and 82.07) corresponding to the

JCPDS file No. of 00-040-12590, and 00-006-0663, respectively. The hydrothermal process and the temperature had a significant transformation effect on the impregnated metals. Peak position at  $2\theta$ = 22.7 corresponds to cellulose (II) was despaired in the XRD spectra of biochar samples that indicate the complete degradation during the gasification process [12]. Also, the metal oxides/hydroxide (M<sup>(+n)</sup>) formed in the impregnated sample were observed to get reduced in their respective elemental state (M<sup>(0)</sup>) after the hydrothermal treatment. The sharp and intense peaks in the BSC-Ni-Ru sample demonstrate the high crystallinity of M<sup>(0)</sup> nanoparticles. The crystalline size of metal nanoparticles calculated using the Scherrer equation was approximately 35 nm and 20 nm for the BS-Ni-Ru and BSC-Ni-Ru samples, which is in close agreement with the particle size calculated from TEM analysis.

# Hydrothermal gasification

Hydrothermal gasification of raw and metal (Ni and Ru) impregnated banana pseudostem was carried out at sub- and supercritical water conditions. The process operating temperature plays a pivotal role in the degradation and gaseous yield of biomass. Thus, process temperature was varied between 300 to 600 °C, and reaction time (60 min.) and biomass-to-water ratio (B: W- 1:10) were kept constant. The gaseous yields of H<sub>2</sub>, CO<sub>2</sub>, and CH<sub>4</sub> increase with the increase in gasification temperature, while the opposite effect was observed for CO gas yield (Fig. 5). Temperature significantly affects the gaseous product, especially H<sub>2</sub>, which increased more than six times after increasing the temperature from 300 °C (H<sub>2</sub>- 2.1 mmol/g) to 600 °C (H<sub>2</sub>- 12.27 mmol/g) (Fig. 5 and Table 2). Initially, at subcritical/near-critical condition (i.e., temp.- 300-400 °C), formation of CH<sub>4</sub> (300 °C- 3.4 mmol/g, 400 °C- 4.82 mmol/g) dominates over H<sub>2</sub> (300 °C- 2.1 mmol/g, 400 °C- 4.15 mmol/g) as the gasification generally proceeds by ionic mechanism and methanation reaction. At elevated temperature (500- 600 °C), reforming reactions along with water-gas-shift reaction accelerate to produce a higher gas yield of H<sub>2</sub> (500 °C- 7.28 mmol/g, 600 °C- 12.27 mmol/g) (Fig. 5 and Table 2).





The presence of metals (Ni and Ru) in the biomass matrix encourages the breakage of complex bonds like C-C, C-O, C-H, etc., and also promotes the degradation of the ring and straight-chain structured components into smaller intermediates [13]. The formation of metal nanoparticle  $(M^{(0)})$  during the volarisation of metal impregnated biomass significantly affect the yield of a gaseous mixture. As a result, H<sub>2</sub> (12.27 mmol/g) of impregnated samples increased almost

threefold compared to the raw biomass (H<sub>2</sub>- 4.2 mmol/g). Nanometals formation also significantly increases the overall gas yield, contributing to the increment in the total gas yield from 13.64 mmol/g to 26.81 mmol/g and carbon gasification efficiency from 46.64 % to 76.65 % as compared to raw biomass, respectively (Table 2).

	<b>Operating Condition</b>	TT	TOV		Biochar
Samples	(BTW Ratio-1:10; 60 min)	H <sub>2</sub> (mmol/g)	(mmol/g)	CGE (%)	(Wt. %)
	300 °C	2.1	9.51	39.06	17.76
BS-Ni-Ru	400 °C	4.15	14.59	55.03	12.57
	500 °C	7.28	19.72	65.58	8.02
	600 °C	12.27	26.81	76.65	5.86
Raw	600 °C	4.2	13.64	46.64	13.51

Table 2. Hydrothermal gasification of raw and metal-impregnated banana pseudostem.

The formation of nanometals ( $M^{(+n)}$ ) in the process of metal impregnation into biomass and their reduction into elemental form ( $M^{(0)}$ ) during the hydrothermal treatment also plays an essential role in the degradation of char/tar. At the highest operating temperature (600 °C), residue generated in the form of biochar was found to be 5.86 wt. %. Thus, almost complete degradation of biomass was achieved following the experimental process described here. Also, a much higher yield of H<sub>2</sub>, TGY, and CGE was achieved for the supercritical water gasification of metal (Ni and Ru) impregnated biomass compared to the raw biomass sample.

# CONCLUSIONS

Banana pseudostem was impregnated with the Ni and Ru metal salts with a motive to boost the hydrogen gas yields and lower down the residue generation. Metals loading was carried out at the pH value of 5.6 (zero-point charge). It was observed that the nanometals  $(M^{(+n)})$  in the impregnated biomass and the transition of metals into  $M^{(0)}$  greatly influenced the overall gas yields, especially hydrogen. Also, almost complete degradation of biomass was experienced during in-situ hydrothermal gasification of metal (Ni and Ru) impregnated biomass. It was also evident from the TEM image and XRD spectral analysis of biochar sample that nanometals  $(M^{(0)})$  having an average particle size of approximately 15 nm are highly dispersed and embedded into the hydrothermally activated char that can be further used as a raw material for the manufacturing of energy storage devices.

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# EXPERIMENTAL INVESTIGATION OF FROST ON AN AIR-SOURCE HEAT PUMP EVAPORATOR

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#### EXTENDED ABSTRACT

#### **OVERVIEW**

The application of heat pumps for buildings heating systems in the cold or transitional season of the year is increasingly common not only in Lithuania but also in other European Union countries. Due to the growing popularity of air to air or air to water heat pumps in the building sector, the problem of evaporator heat exchanger freezing is also increasing in importance. As the outdoor temperature drops, the heat pump's efficiency – coefficient of performance for heating (COP) decreases. At high relative humidity there is also a risk of the evaporator heat exchanger to start freezing. This increases the energy consumption of the system, has a negative effect on heat exchange. Given the need for experimental and numerical research, the aim of this work is to analyse and present the characteristics of air source heat pump (ASHP) in the presence of the risk of freezing and to qualitatively assess the COP reduction due to frost formation. This paper investigates the operation of an ASHP in the cold season, observes the freezing of the evaporator as environmental conditions change. An experimental stand was constructed for this research; the necessary measuring devices and a camera were installed for visual observation of the experiment and assessment of frost formation. The experiments were carried out during the transitional - cold season of the year. It was found that frost formation on the evaporator started when the outdoor temperature was <3.5 °C and the relative humidity reached 88%. The defrost cycle took an average of 5 minutes. The impact of evaporator freezing on the operation and efficiency of the system - COP - has been assessed.

#### METHODOLOGY

The object of the research is an evaporator of the ASHP Panasonic WH-UD07HE5-1, located in the Laboratory of Building Energy and Microclimate Systems of Vilnius Gediminas Technical University. The operation mode of the heat pump heating circuit during the cold season of the year is analysed. The conditions under which the frost layer begins to form on the evaporator including the peculiarities of its formation and influence on the operation mode and efficiency of the – ASHP are investigated. According to the manufacturer's specifications, the heat output of the ASHP is 7 kW, and the COP is 4.46 when the ambient air temperature is 7 °C and the secondary circuit supply water temperature is 35 °C. The design air flow rate of the evaporator is 2760 m<sup>3</sup>/h.

Temperature, humidity, air flow rate, ambient air parameters were measured during the experiment. In addition, a video camera (GoPro HERO7 Silver) mounted under the hood perpendicularly to the heat exchanger was used for visual observation of the experiment and assessment of the frost formation. All measurement results were recorded every 1 minute.

From the ASHP experimental operation data, its efficiency factor for heating – COP – was calculated as the ratio between the amount of heat received by the heat pump and the electricity consumption. The amount of electricity consumed by the heat pump was calculated knowing the current, voltage and duration of the experiment. The power factor  $(\cos(\varphi))$  was taken 0.97. The amount of heat received by the heat pump in the external unit (secondary - water circuit) was calculated knowing the measured water flow rate, temperature difference between supply and return temperatures in the water circuit, water density and specific heat capacity at constant pressure.

During the recording of heat pump operation data and visual monitoring of its evaporator, the data was analysed to examine the defrosting process of the heat exchanger and to assess the reduction in COP

due to frost formation on the evaporator. Depending on the ambient weather conditions during the experiments, it was decided to distinguish three different periods when the typical days have such temperatures and humidities:

- 1) positive average ambient temperature (~4°C) and average relative humidity (~86%);
- 2) negative ambient temperature (from -7 to  $-1^{\circ}$ C, about  $-3^{\circ}$ C) and average relative humidity (~93%);
- 3) average temperature about (0°C) and average relative humidity (~95%).

#### RESULTS

The experiments were performed during the 2020 heating season. Three different periods are selected for the analysis: from November 11, 5 p.m. to November 12, 1 p.m.; from December 1, 5 p.m. to December 3, 2 p.m.; and from December 15, 4 p.m. to December 17, 1 p.m.

These periods were chosen because at that time frost formation was observed on the evaporator of the heat pump, and the heat exchanger defrosting processes occurred. The set parameters for the supply and return water temperature in the external heat pump unit were 50 °C and 45 °C, respectively. Figure 1 shows a comparison of the results for all three time periods.



Fig. 2 Comparison of all three periods – variation of air flow and COP depending on ambient temperature and relative humidity. 1 - average ambient temperature 4.02 °C, relative humidity 85.82 %; 2 - average ambient temperature 0.51 °C, relative humidity 94.90 %; 3 - average ambient temperature -2.80°C relative humidity 92.54 %;

#### CONCLUSIONS

With the popularity of ASHP installations in cold and temperate climates, there is a need to assess the impact of climatic conditions on the operation of such equipment - efficiency. The article experimentally and visually examines the effect of air source heat in the presence of negative, about 0 °C and positive ambient air temperature, when there is a risk of freezing the heat pump evaporator. Experiments have shown that:

- 1. Frost formation on the evaporator's heat exchanger plates starts when the outdoor air temperature is less than 3.5 °C and the relative humidity reaches 88%.
- 2. The frozen evaporators defrost cycle takes an average 5 minutes. The defrost cycle remains the same during the different experiments, regardless of the ambient air parameters, only its frequency varies.
- 3. The frost defrost process alone reduces the COP by 10.74% compared to the same period as evaporator freezes but defrost process does not happen. In other cases examined the COP has fallen even more (up to 20.99% the average ambient air temperature was -2.80 °C).
- 4. During the experiments, the dependence of the extracted air flow on the ambient air temperature is observed. The average air flow rate is found to decrease as the ambient temperature rises.

Keywords: heat pump, evaporator, frost formation, efficiency, experiment, transitional - cold season.

# AN EFFICIENT PV POWERED BATTERY CHARGING DC GREEN PLUG SCHEME

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#### ABSTRACT

Renewable energy sources and robust low impact power electronic interfacing applications are getting significant use in emerging green energy use and efficient utilization. Significantly, the use of low power residential/commercial photovoltaic (PV) energy with limited storage devices reduces the total price of distributed generation (DG) systems. The power electronic DC to DC and DC to AC converters serve the efficient energy transfer from PV to battery V2H (Vehicle to home) /V2G (Vehicle to grid). At this point, some flexible alternating current transmission devices (FACTS) and more effective controllers. The use of green is based on using the green plug filter on DC side to reduce inrush current conditions and transient over-voltages during the charging mode and recover energy via freewheeling diode during pulse width switching of DC to DC converter.

In this paper, a novel low cost decoupled PV – powered boost converter device is used with a green plug filter to feed the battery. The proposed green plug and DC-DC boost converter are switched with a pulse with modulation (PWM) strategy. These signals are generated by proportional integral derivative (PID) offline gain optimized PID control and driven by an error signal from a hybrid time descaled dual loop controller. The scaled time decoupled control loops use the current and voltage error signals to obtain the total error. The digital simulation models are designed in MATLAB/Simulink software and discussed for various operating conditions. The digital simulation results validated the robustness and efficient operation of the green plug filter. The proposed V2H battery charging PV powered scheme provides better energy-efficient utilization and fast charging with reduced DC inrush current and voltage transient conditions with different selected hybrid charging weighted modes.

**Keywords:** Photovoltaic array, V2H Battery charging, Boost converter, Dual loop controller, PV energy utilization, DC green plugs, FACTS

#### **INTRODUCTION**

The renewable photovoltaic sources and their emerging use in energy storage applications for battery and hybrid storage devices are essential with time and research by more scientists [1-3]. The power electronic converters and their controllers are the fundamental part of the hybrid storage systems. These components transmit the generated energy from PV sources to storage devices or the grid [4, 5]. Also, some FACTS components increase the efficiency of the general system. For example, a DC green plug FACTS system which is includes switched capacitor compensated shame, is proposed with a converter to increase the general system efficiency in some applications [6,7]

PV array operating efficiency changes based on solar irradiation and temperature level. Also, these sources are nonlinear and act depending on the I-V characteristic of the PV source. This nonlinearity is affected by the efficiency of the PV panel [8]. To increase the efficiency required to work in the maximum power point of PV panels. It is possible to use some controllers and converters to connect the PV panel's output [5, 9]. Also, it is required to supply joint bus stabilization for efficient battery charging. A supercapacitor (SC) and FACTS system can be proposed as a solution [9, 10, 11]. In a paper, a new distributed FACTS-based green plug-switched filter capacitor (GP-SFC) filter is presented for efficient utilization of microgrid-connected wind energy systems [12]. In another paper, a FACTS based dynamic switched C-type filter (DSCTF) compensator scheme for distribution systems is presented with different load characteristics and control strategies [13]. Supplementary control laws applied to the existing FACTS devices to improve the damping of oscillations in power systems. These additional actions are referred to as power oscillation damping (POD) control [14].

A paper presents many online error-driven control strategies for a hybrid PV-FC-dieselbattery powered system for EV. The proposed regulation schemes include PID modified control strategies and dynamic variable structure sliding mode control scheme [15]. On the other side, a book chapter discusses advances in intelligent control systems and their micro-energy grids applications [16]. Moreover, another paper presents a fuzzy logic modified multi-stage hierarchical Fuzzy Logic PID control scheme for a hybrid AC grid-drive- PV-battery charging system [17]. A practical single phase induction motor controller based on the multi-objective genetic algorithm (MOGA) with some green plug compensator schemes is given with low-cost compensator schemes [18]. A novel, fully controlled, flexible, and self-adjusting LED lighting PV-Battery powered system using sinusoidal pulse-width modulation (SPWM) switching is presented in another paper. A dual-loop error-driven controls this scheme, time descaled, weighted modified proportional-integral-derivative (WM-PID) control scheme for the photovoltaic (PV)-battery interfaced to the light-emitting diode (LED) lighting load [19, 20].

The paper presents a total low-cost V2H battery charging scheme using a dc green plug filter PWM - switched multi-loop hybrid regulation controller. This controller uses the battery, PV and common bus dc voltages and currents to produce control loop error signals and drive PID controllers. The PID outputs used the generate PWM switching signals. The main idea and proposed PV powered green plug scheme is given in this paper, as shown in Fig. 1. The controller design steps and controller components are given more detailed in this study. The digital simulation model is done using MATLAB/Simulink, and digital simulation results are presented for some operating conditions.

#### THE PROPOSED EFFICIENT PV POWERED SCHEME

The paper presents a PV powered scheme for battery charging using a Green Plug-Supercapacitor DC interface filters scheme, as shown in Figure 1. The green plugs act as super storage and DC side filter to reduce voltage transients and DC inrush current conditions. The operation uses MOSFET/IGBT switched green plug dc capacitors controlled by the dual regulating decoupled and descaled controller. The free-wheeling energy recovery diode  $D_B$  ensures energy exchanges between source and Li-Ion battery loads during energization / de-energization. The boost type DC-DC converter is controlled using an integrated V-I-P weighted charging controllers with assigned weighting. It ensures descaling and best hybrid fast charging modes using selected loop-weights to reduce transients on the DC side and ensure energy-efficient operation.



Fig. 1. V2H Battery-powered PV - Green Li-Ion Plug - Interface scheme.

The proposed green plug filter is combined with a PV model, a boost converter, battery and green plug filter components. The PV model is designed using the PV model equation in MATLAB/Simulink, as shown in Figure 2(a). This model is designed, tested and used previously by the authors [8, 19, 20]. The green plug filter compensator model is given in Figure 2(b). This green plug filter compensator is connected between the boost converter's input and output to compensate the boost converter's input and output filter capacitors. The central part of this scheme is the boost converter required to increase and regulate the PV source voltage to energies the battery or other loads. The boost converter is shown in Figure 2(c). This switching converter includes a series inductance with the source and increases the input voltage at the output. The battery model is designed using MATLAB/Simulink, as shown in Figure 2(d). The battery model uses the Lead-acid battery equations, Lithium-Ion, Nickel Cadmium and Nickel Metal Hydride type and adjust the nominal voltage, rated capacity, the initial state of the charge response time.





## THE CONTROLLER DESIGN STEPS AND STRUCTURE

The dual regulating controller shown in Figure 3 is a coupled version using energy freewheeling exchanges from the load battery side and the PV input side with the green plugs scheme to reduce transients and inrush conditions on the DC system. It is essential to ensure all loops' best weightings reduce interactions that may result in sudden inrush DC transients by describing and enhancing major and minor loop functions in the battery charging regulator controlling. The PWM switched DC-DC boost converter for Li-Ion battery charging load and the second regulator controlling the DC green plug filter PWM. The weighted extra modulation loop for the inter-coupled free wheel exchange current error I<sub>DB</sub> is added to ensure a proper energy balance of DC power exchanges.



Fig. 3. The Full structure of the dual regulation loop-decoupled controllers.

The dual loop\_1 and dual loop\_2 regulators and current boost supplementary loop regulators designed in MATLAB/Simulink are shown in Figure 4 (a, b, c). This loop generates error signals ( $e_1$ ,  $e_{t2}$ ,  $e_{ldb}$ ) that drive PID\_A and PID\_B controllers. The current loop regulators error signal is added with dual-loop regulators errors signals to amplify the error signals. At last, the two PID controller output signals are used to generate switching PWM1 and switching PWM2. One of these switching signal ( $S_C$ ) drives the converter, the other ( $S_f$ ) drives the green plug filter compensator.



Fig. 4. The MATLAB/Simulink models of; (a) Dual loop 1, (b) Dual loop 2, (c) Current boosting supplementary circle.

# DIGITAL SIMULATION RESULTS

The simulation results are obtained in the MATLAB/Simulink functional model, as shown in Fig. 5.



Fig. 5. The Functional block of the V2H battery charging scheme in MATLAB/Simulink.

The digital simulation results are shown in Figs. 6-8. The battery load side current ( $I_B$ ), voltage ( $V_B$ ) and power variations ( $P_B$ ) for solar irradiation ratio (Sx=100%) and state of charge (SOC=90%) are seen in Figure 6(a). The PV side current ( $I_{PV}$ ), voltage ( $V_{PV}$ ) and power variations ( $P_{PV}$ ) with time for Sx=100% and SOC=90% are seen in Figure 6 (b). The voltage and current variations in the PV side and battery side are stable with time. However, there were negative currents from the battery to the converter, and the current flows from the PV to the battery with time. The PV voltage is increased with time to charge the battery. The power flow is constant with time from the PV to battery load time, and more than 90% of PV power charges the battery.



Fig. 6. Digital simulation results of the battery (a) PV (b), voltage, current and power variations for Sx=100% and SOC=90%.

The battery load side current, voltage and power variations for Sx=100% and SOC=10% are seen in Fig. 7(a). The PV side current, voltage and power variations with time for Sx=100% and SOC=10% are seen in Figure 7(b). The battery load side current, voltage and power variations for Sx=50% and SOC=50% are seen in Fig. 7(a). The PV side current, voltage and power variations with time for Sx=50% and SOC=50% are seen in Figure 7(b). The voltage and current variations in the PV side and battery side are stable with time and it is suitable the charge the battery in all states.



Fig. 7. Digital simulation results of the battery (a) PV (b), voltage, current and power variations for Sx=100% and SOC=10%.



Fig. 8. Digital simulation results of the battery (a) PV (b), voltage, current and power variations for Sx=50% and SOC=50%.

# CONCLUSIONS

An efficient PV powered V2H robust, low-cost battery charging scheme that uses a DC green plug efficient energy storage scheme is validated in this paper. The proposed efficient PV powered V2H scheme and the basic modules are discussed with a modified multi-regulations descaled decoupled PWM controller. The dual regulation multi-loop controller design and basic structure are given more detailed. The digital simulation model and results are shown in MATLAB/Simulink in this paper. The digital simulation results validated an efficient utilization of the V2H battery charging scheme. The same method is extended to a large scale (150-500 kW) commercial V2G hybrid multi-source grid-PV-Fuel cell system. The option of selected weighting charging modes using descaled multi stage regulation loops within the controllers ensure smooth fast energy efficient charging.

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| APPENDIX | A: Designed | DC System | Parameters |
|----------|-------------|-----------|------------|
|----------|-------------|-----------|------------|

PV Array Parameters				
PV voltage (DC)	220 V			
PV power	300 kW			
R <sub>d</sub>	0.1 Ω			
L <sub>d</sub>	50-100 mH			
Battery Par	ameters			
Battery model	Lithium-Ion			
Battery voltage	240 V (nominal)			
Battery rated capacity	240 Ah			
Line and Boost Converter Parameters				
S <sub>a</sub> , S <sub>b</sub> , S <sub>c</sub> MOSFET switche				
C <sub>d</sub>	100 mF			
R <sub>a</sub>	0.01 Ω			
La	50 mH			
Св	100 F			
C <sub>fD</sub> 6500 u				
C <sub>fB</sub>	6500 uF			

**B:** Controller Gain Parameters

Dual Loop Controller Parameters				
V <sub>D_base</sub>	300 V			
I <sub>D_base</sub>	800 A			
K <sub>D1</sub>	0.5			
K <sub>D2</sub>	0.25			
WM-PID Controller Parameters				
KP	0.2			
Kı	0.02			
K <sub>D</sub>	001			
Switching frequency(f <sub>sw</sub> )	2500 Hz			

# INFLUENCE OF THE WORKING MEDIUM COMPRESSIBILITY ON THE DETERMINATION OF IDLE OF AN AXIAL TURBINE STAGE WITH A LARGE FANNING

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#### ABSTRACT

At present, the high-power turbines are used to regulate the load on power grids. The last stages have blades of a limited length in the low-pressure cylinder of these turbines. These stages operate in power consumption mode below the idle mode. Therefore, the determination of the idle mode of such stages has great and practical importance in determining the range of the turbine operation.

The idle mode criterion is the relative volumetric flow rate. The last stages of powerful steam turbines are designed and operated at large Mach numbers at the outlet of rotor blades. The operation of the stage at the idle mode occurs at subsonic velocities.

Experimentally, the idle of stages with a large elongation of the blades is determined by studying models of turbine stages in the air with Mach numbers less than 0.35. This corresponds to the condition of the incompressibility of the working medium. Therefore, it is necessary to develop a methodology for determining the effect of compressibility on the characteristics of the idle mode.

The solution to this task includes two questions: an estimate of the conditions for transferring modelling on an incompressible medium to the operation of a full-scale stage with a steam (compressible) medium; an estimate of the influence of the ratio of specific steam volumes behind and in front of rotor blades on the relative volumetric flow rate corresponding to the idle mode of the stage.

This task is considered in a one-dimensional formulation. The methodology for determining the idle mode of stages with a large fanning is proposed. It includes the analysis of the ratio of specific volumes as a factor of the compressible medium. The dependence is obtained for estimating the influence of compressibility at the function of effective angles of flow exit from the stage blades.

**Keywords:** large fanning, influence of compressibility, working medium, idle mode, relative volumetric flow, Mach numbers, low-pressure cylinder.

### **INTRODUCTION**

Recently, the load regulation of the power grid is carried out using high-power turbines. At the same time, they operate in a wide range of changes in electrical power. The last stage, behind which the condenser is located, enters the power consumption mode first when the turbine load decreases.

The last stages with a large fanning, at which the active length of the working blade is 0.7 - 1.44 m for high-power turbines. With such a length, even before the idle of the stage, a flow separation occurs behind it [1]. This leads to a structural rupture of the flow in the stage with a large fanning and influences of the reliability of the idle mode determination.

There are a few published works devoted to both experimental studies of idle modes [2, 3], as well as theoretical works of the authors [4, 5], where the theory of the movement of the working medium is in a one-dimensional formulation. In this case, the movement of an axisymmetric flow limited by solid cylindrical surfaces is considered. This methodology permits to get the satisfactory results for high and medium pressure cylinder stages [4]. At the

same time, it is hardly applicable for stages of low-pressure cylinders (LPC) with a large fanning.

There is a sharp increase in specific volumes of steam in the last stages of steam turbines at low absolute pressures in the condenser. This leads to an increase in the passage area of the channels in the stator blades (SB) and the rotor blades (RB) and, as a result, this leads to an increase in the length of the blades to the limiting values. The transition to the conical shape of the stages in LPC causes a restructuring of the flow during the formation of a supersonic flow at the outlet of the channels of SB and RB, which affects the increase in the flow exit angles due to the flow rotation in the oblique cut of the channels. Such processes take place in a compressible working medium.

The aim of this study is a methodological approach to determining the influence of the compressibility of the working medium on the characteristics of the idle mode of the stages with a large fanning, which are operating in a steam medium at low absolute pressures.

# THE DETERMINATION OF THE IDLE MODE OF THE STAGE

A dependence was obtained to determine the idle mode of stages with cylindrical meridional bypasses for a compressible working medium (steam at low pressure) based on the use of the Euler turbine equation, the theoretical determination of the efficiency at the stage rim and equating it to zero ( $\eta_u = 0$ ) [6] in the form

$$\overline{Gv_{2}}_{id} = \frac{\left(\frac{u}{C_{0}}\right)^{2}_{nom}}{\left(\frac{u}{C_{0}}\right)^{2}_{nom} + \frac{1}{2}\left(\frac{v_{2}}{v_{1}}\right)_{nom} \cdot \eta_{u_{nom}}},$$
(1)

where  $\overline{Gv_{2_{id}}} = \frac{Gv_{2_{id}}}{Gv_{2_{nom}}}$  is the relative volumetric flow rate at the outlet of RB stage (section 2);  $Gv_{2_{id}}$  is the volumetric flow rate of the working medium through the stage at its idle mode;  $Gv_{2_{nom}}$  is the volumetric flow through a stage at the nominal operation mode, which corresponds to the maximum efficiency  $\eta_{u_{max}} = \eta_{u_{nom}}$  at the stage rim;  $\left(\frac{u}{C_0}\right)_{nom}$  is the characteristic number at the nominal stage operation mode;  $\left(\frac{v_2}{v_1}\right)_{nom}$  is the ratio of specific volumes behind RB and in front of it (in a rim clearance, section 1) at the nominal stage operation mode.

Based on a sample of thermal calculations of several high-power steam turbines, which are considered with the involvement of special programs used in the design of the turbine, the characteristics  $\frac{u}{C_0}$ ,  $\eta_u$ ,  $\frac{v_2}{v_1}$  were selected, according to which a methodological approach was constructed in a one-dimensional formulation to determine the idle mode of stages with a large fanning.

The equation (1) was obtained for a real working medium with a cylindrical flow in a stage and under the condition that it occupies the entire outlet section at an axial flow exit from the rotor blades.

The factor of compressibility of the working medium is the ratio of the specific volumes of steam  $\left(\frac{v_2}{v_1}\right)_{nom}$ . The strongest influence of compressibility occurs at flow speeds exceeding the critical speed (the speed of sound). These speeds appear at large thermal drops, which triggered in RB and SB of the stage.

It should be noted that when determining the ratio  $\left(\frac{v_2}{v_1}\right)_{nom}$ , two values of the specific volume can be considered as  $v_{2nom}$ : in the supersonic flow behind RB and in the throat (critical) section of the channel  $v_{2th}$ , which remains constant at the supersonic flow.

The ratio  $\left(\frac{v_{2\text{th}}}{v_1}\right)_{\text{nom}}$  characterizes the flow component of the stage, which is associated with the geometric (effective) angle  $\beta_2^{\text{eff}}$  of the flow exit from RB. This angle doesn't depend on the stage operation mode both in the supersonic and subsonic modes of the medium flow in the channels of RB.

The flow becomes incompressible for the ratio  $\left(\frac{v_2}{v_1}\right)_{\text{nom}} \cong 1.0$  and taking into account the equation (1), the value  $\left(\overline{Gv_2}_{\text{id}}\right)^{\text{incom}}$  is determined as follows

$$(\overline{Gv_2}_{id})^{incom} = \frac{(u/c_0)^2_{nom}}{(u/c_0)^2_{nom} + \frac{1}{2}\eta_{u_{nom}}}.$$
 (2)

The influence of compressibility on the value of  $\overline{Gv_2}_{id}$  can be determined through the ratio  $\overline{Gv_2}_{id} / (\overline{Gv_2}_{id})^{incom}$ . For this, the numerical study of this ratio was carried out in the range of  $1.0 \le \left(\frac{v_2}{v_1}\right)_{nom} \le 4.0$ , which corresponds to the real range for the last stages of steam turbines. Since the ratio  $\left(\frac{v_2}{v_1}\right)_{nom}$  depends on the degree of the stage reaction, which forms the difference in flow outlet angles  $\alpha_1$  and  $\beta_2$ , then its (the value  $\left(\frac{v_2}{v_1}\right)_{nom}$ ) should be considered as depending on the function of angles  $\left(\frac{\sin\beta_2}{\sin\alpha_1} - 1\right)$ .

The results of the numerical study of four stage models [5] for which the known values of  $\left(\frac{u}{C_0}\right)_{\text{nom}}$  and  $\eta_{u_{\text{nom}}}$  are shown in Fig. 1. The characteristics of these values are given in Table 1.

Stage	$\left(\frac{u}{C_0}\right)_{\text{nom}}$	$\eta_u$	$\alpha_1^{\rm eff}$	$\beta_2^{\rm eff}$	$D_{\text{med}/l}$	$\Theta = {l / D_{\text{med}}}$
Ι	0.67	0.716	22°	22°53′	2.58	0.388
II	0.675	0.740	22°	24°	2.87	0.348
III	0.61	0.757	22°	25°18′	3.24	0.309
IV	0.54	0.748	22°	27°50′	4.57	0.219

Table 1 - Geometric characteristics of the models last stages with a large fanning

The stages I and II were also tested with a conical peripheral meridian bypass, the angle  $\gamma_m$  of which is 30° and 50°, respectively.

The graphs shown in Fig. 1 are approximating by a power dependence of the form

$$\frac{\overline{Gv_{2}}_{id}}{\left(\overline{Gv_{2}}_{id}\right)^{incom}} = 1 - 0.35 \left(1 + 0.1\sqrt{tg\gamma_{m}}\right) \left[\left(\frac{v_{2}}{v_{1}}\right)_{nom} - 1\right]^{0.48}.$$
 (3)



Fig. 1 Influence of the compressibility of the working medium on the determination of the idle characteristic of the stages with a large fanning

The values of the specific volumes  $v_2$  and  $v_1$  of the working medium (steam) behind the trailing edges of the blades SB and RB for dependence (3) are taken.

To use the equation (3), it is necessary to have the dependence  $\frac{v_2}{v_1}$  as a function of the angle characteristics of the flow that passes through the stage.

The value of the ratio  $\left(\frac{v_2}{v_1}\right)_{nom}$  is taken during design and is usually unknown under operating conditions, which does not allow using this dependence directly. The performed estimate of the influence of this ratio for the last stages of several operating turbines showed that the use of this dependence, due to the assumptions made in the theoretical methodology, gives a significant discrepancy with the real values. Therefore, the following methodology is considered to determine the idle mode of stages with a large fanning.

#### METHODOLOGICAL APPROACH TO DETERMINATION OF THE IDLE

The efficiency  $\eta_{u_{\text{nom}}}$  at the rim of the stage is determined by the energy losses in the channels of SB  $\xi_{\text{SB}}$ , the channels of RB  $\xi_{\text{RB}}$  and the runaway velocity  $\xi_{\text{rv}}$  and is written as

$$\eta_{u_{\rm nom}} = 1 - \xi_{\rm SB} - \xi_{\rm RB} - \xi_{\rm rv}.$$
 (4)

The losses  $\xi_{\text{SB}}$ ,  $\xi_{\text{RB}}$  (kinetic losses) in the nominal mode are constant. For the last stages of steam turbines, they are in the region of self-similarity of the flow by the Reynolds number  $Re_{C_1}$  and  $Re_{W_2}$  ( $Re_{C_1}$ ,  $Re_{W_2} > 10^5$ ) and they have the limited value. The main influence on the value of  $\eta_{u_{\text{nom}}}$  is exerting by losses with the runaway velocity  $\xi_{\text{out}} = {\binom{C_2}{C_0}}^2$ , where  $C_2$  is the velocity at the exit from RB;  $C_0$  is the fictitious (theoretical) velocity, corresponding to the heat drop triggered in the stage  $H_0$ ,  $C_0 = \sqrt{2H_0}$  [7].

The losses with the runaway velocity for the last stage are lost beyond retrieve, therefore, when designing a stage, they should be minimal. The axial outlet of the stage corresponds to this condition, i. e. the outlet angle  $\alpha_2$  should approach to 90° as much as possible. Such a stage

is optimal and has a maximum efficiency  $\eta_{u_{nom}}^{max}$  at the rim of the stage. Consequently, the degree of reaction and the associated function of the outlet angles must be chosen such that they ensure the optimal operation of the stage ( $\alpha_2 \approx 90^\circ$ ) at the nominal mode.

Analysis of available characteristics of operated at power plants high-power steam turbines (K-800-240, K-300-240, T-250/300-240, K-200) and the designed versions of their various modification options (K-210, K-225 [8]) showed that, in the first approximation, it is possible to use the dependence of the form adopted for the modes  $M_{C_1}$  and  $M_{W_2} \le 1.0$ 

$$\left(\left(\frac{v_2}{v_1}\right)_{\text{nom}} - 1\right) \sim \left(\frac{\sin\beta_2^{\text{eff}}}{\sin\alpha_1^{\text{eff}}} - 1\right).$$
(5)

The form of dependence (5) is shown in Fig. 2 and can be represented by the equation

$$\left(\left(\frac{v_2}{v_1}\right)_{\text{nom}} - 1\right)_{\text{opt}} = 1.4 \left(\frac{\sin\beta_2^{\text{eff}}}{\sin\alpha_1^{\text{eff}}} - 1\right).$$
(6)

The characteristics of the stages which are corresponding to dependence (6) were obtained for optimally designed stages with an axial or close to it ( $\alpha_2 = 85^\circ \div 101^\circ$ ) the outlet flow from RB.



Fig. 2 Dependence of the compressibility function on the value  $\left(\frac{\sin\beta_2^{\text{eff}}}{\sin\alpha_1^{\text{eff}}} - 1\right)$ 

Some scatter of points, to all appearances, is associated with the flow deviation from the axial direction and the error in determining the specific volumes of the working medium at pressure

 $P_{2\text{th}} = \varepsilon_{\text{cr}} \cdot P_1$ . The value  $\varepsilon_{\text{cr}} = 0.577$  is taken for the saturated steam with the adiabatic exponent  $\kappa = 1.135$ . Losses from moisture in the channels of RB were not considered.

Thus, the dependence (3) after substitution (6) will take the form

$$\frac{\overline{Gv_2}_{id}}{(\overline{Gv_2}_{id})^{incom}} = 1 - 0.49 \left(1 + 0.1\sqrt{tg\gamma_m}\right) \left[\frac{\sin\beta_2^{eff}}{\sin\alpha_1^{eff}} - 1\right]^{0.48}.$$
(7)

The determination of the characteristics of the idle mode of the stage with a large fanning is possible with a known relative volume  $(\overline{Gv_{2}}_{id})^{incom}$  during the operation of an incompressible working medium, which can be obtained either experimentally or by calculating the three-dimensional flow of a viscous medium for the nominal stage operation mode.

#### **MODELING CONDITIONS**

Account must be taken of the simulation conditions when determining  $\overline{Gv_2}_{id}$ . If the relative volumetric flow rate is obtained experimentally under conditions of incompressibility of the working medium (air) and the stage operates on a steam, then it is necessary to consider the modeling conditions: the geometric similarity of model and full-scale stages; the kinematic similarity  $\binom{u}{C_0}_{ful} = \binom{u}{C_0}_{mod}$ . The ratio of volumetric flow rates of full-scale  $V_{ful}$  and model  $V_{mod}$  of stages is equal

The ratio of volumetric flow rates of full-scale  $V_{\text{ful}}$  and model  $V_{\text{mod}}$  of stages is equal to [9]  $\frac{V_{\text{ful}}}{V_{\text{mod}}} = \sqrt{\frac{H_{\text{ful}}}{H_{\text{mod}}}}$  under these modelling conditions or for relative volumetric flow rates

$$\frac{\overline{V}_{\text{ful}}}{\overline{V}_{\text{mod}}} = \sqrt{\frac{\overline{H}_{\text{ful}}}{\overline{H}_{\text{mod}}}},\tag{8}$$

where  $\overline{H} = \frac{H}{H_{\text{nom}}}$  is the ratio of heat drops for the considered idle mode and the nominal mode, respectively.

The adiabatic exponent is  $\kappa = 1.4$  for the working medium (air) with Mach numbers  $M_{C_1}$ ,  $M_{W_2} < 0.35 \div 0.4$ . The adiabatic exponent  $\kappa = 1.135$ , when working with the wet steam (degree of dryness x < 1).

The heat drop of the working medium is defined as

$$H = \frac{\kappa}{\kappa - 1} R T_0 \left( 1 - \left(\frac{P_2}{P_0}\right)^{\frac{\kappa - 1}{\kappa}} \right).$$
(9)

The influence of the adiabatic exponent on the heat drop and, as a consequence, on the volumetric flow rate can be determined as follows

$$V \sim \sqrt{\frac{\kappa}{\kappa - 1} R T_0 \left( 1 - \left(\frac{P_2}{P_0}\right)^{\frac{\kappa - 1}{\kappa}} \right)}$$
(10)

with the same stage parameters.

#### **RESULTS OF THE STUDY**

There is the pressure before stage  $P_0 = 25$  kPa, the pressure after stage  $P_2 = 5$  kPa and the steam temperature before stage  $t_0 = 62$ °C are taken as an example for the last (31st) stage of T-250/300-240 turbine which is operating in the saturated steam.

Applying the dependence (10) with consideration to the above parameters and at  $\kappa = 1.4$  $V_{air} \sim 352.29$ , at  $\kappa = 1.135$   $V_{steam} \sim 476.39$ . The ratio  $\frac{V_{steam}}{V_{air}} = 1.3523$  or  $(Gv_2)_{steam} = 1.3523 (Gv_2)_{air}$ .

The use of relative volumetric flow rates for air and steam at  $P_{0id} = 18$  kPa,  $t_0 = 47^{\circ}$ C with a similar methodology gives the value  $(\overline{V}_{air})_{id} = (\overline{Gv_2}_{id})^{air} = 0.891$  and  $(\overline{V}_{steam})_{id} = (\overline{Gv_2}_{id})^{steam} = 0.880$ . Their ratio is  $(\overline{Gv_2}_{id})^{air} = 0.9877 (\overline{Gv_2}_{id})^{steam}$ .

Therefore, the presented methodology to determining the idle mode (7) allows using the relative volumetric flow rates of the idle mode with practically no correction for the properties of the working medium.

The presented results of the influence of compressibility on the idle mode characteristics show that to determine  $\overline{Gv_{2}}_{id}$  stages with a large fanning, it is necessary to have reliable experimental data obtained in the study in an incompressible medium.

### CONCLUSIONS

For the first time, the methodological approach is proposed for determining the idle mode of stage with a large fanning, which is used as the last stage in high-power steam turbines and the influence of the compressibility of the working medium in the form of the ratio of specific volumes specified in the design of the stage at the nominal mode of its operation is considered.

It is shown that to consider the compressibility of the working medium, the specific volume of steam in the throat section of the channels of SB and RB should be taken as a characteristic value.

The dependence is obtained that connects the ratio of specific volumes in the channels of RB at the middle radius for the nominal mode with the function of the effective angles of the flow out of SB and RB.

It is shown that for the relative volumetric flow rate of the idle mode, the results of its determination in the air can be transferred to operation with the wet (saturated) steam practically without corrections for the properties of the working medium.

Computational studies have shown that the discrepancy between the values of the relative volumetric flow rate  $\overline{Gv_2}$  when the stage operates in steam and air does not exceed 1.5% when modeling condition the stage with a large fanning.

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# LOW COST HOME ENERGY MANAGEMENT BASED ON CHARGE TARIFF AND APPLIANCE OPERATION TIME

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#### ABSTRACT

With the rapid decrease in unit energy generation cost of a typical solar photovoltaic system, it has been one of the most attractive ways for hybrid energy generation in residential buildings. The economic performance of such a system usually depends on the solar energy potential at the site of a location where it is installed, additional energy generation and storage systems such as a wind turbine, battery bank, etc., and whether it is on-grid or off-grid. Besides the installation, operation, and maintenance costs of the system, the nominal power of the electrical household appliances, the operation periods and time intervals, the electricity tariff used are also very influential on the economic cost of this system. In order to reduce the daily energy cost depending on the tariff used, electrical household appliances are operated in the time period when the electricity price is the lowest, but this leads to overloads on the power line and damage to the line in the long-term operation. In this study, an approach based on bicriteria genetic algorithms optimization is proposed to reduce both cost and peak power demand to acceptable level for daily basis of home energy management. Preliminary results indicate that the proposed method is meaningful and encouraging to meet the requirements set by householders. This is to be fully amplified in the full paper.

**Keywords:** Energy efficiency, home energy management system, power scheduling, multi-objective optimization.

#### NOMENCLATURE

- *t* :time slot number
- T :maximum time slot number which is 288
- *n* :total number of household appliances

A :total number of non-time shiftable household appliances

B :total number of fully time shiftable household appliances

C :total number of partially time shiftable household appliances

*D* :total number of power shiftable household appliances

e(t) :unit electricity price at t time slot

- $\Delta t$ :hourly length of each time slot
- $L^t$  :power demand for total house appliances at t time slot

*PPD* :peak power demand

- $P_a^t$ : power demand for appliance *a* at *t* time slot
- $U_a^t$ :power of non-time shiftable appliance a
- $X_b^t$  :power of partially time shiftable appliance b

 $Y_c^t$ :total power of fully time shiftable appliance c

 $Z_d^t$ :total power of power shiftable appliance d

 $B_a^t$  :binary digit for appliance a at t time slot

 $\omega_1$  : first weight coefficient

 $\omega_2$  :second weight coefficient

#### **INTRODUCTION**

Electricity is being provided to almost 80% of the world's population. Despite the development in the field of renewable energy, there is an increase in the use of modern devices such as heaters, air conditioners, hybrid electric vehicles, and heat pumps, etc., which leads to an increase in energy consumption. Therefore, the use of electricity generated needs to modernize the electrical system. This is still increasing due to the adaptation of modern lifestyle and easy access to the globe. This has increased the demand drastically. Electricity generation, transmission distribution, and their controls are performed at grid stations. Utility companies usually introduce dynamic pricing policies to control consumers' energy consumption patterns. Electricity unit price regularly escalates in many countries every year due to various reasons such as increased input costs, regional political conflicts, etc. This inevitably leads to increase energy costs of the residents day by day and generating power by a proper photovoltaic system or a hybrid one can be one way to reduce these energy costs. As the smart grids gradually widen and the controllability of household appliances increases, it is possible to reduce both the daily cost of the energy supplied from the grid under certain tariffs and power loss in transmission lines on the basis of the demand-side management strategies. There are different types of pricing schemes which are critical peak pricing, time of use pricing (ToU), low price for offpeak hours, day-ahead pricing and also real-time pricing. Price based demand-side management (DSM) and incentive-based DSM schemes are the two different DSM approaches. In the pricebased DSM scheme, residential consumers shift their controllable devices from peak hours to off-peak hours through the price signal. In the incentive-based DSM scheme, there is a contract between utility companies and consumers. In this scheme, utility companies can centrally control the users' appliances by providing impressive incentives.

### LITERATURE REVIEW

Recently, there have been many studies based on popular deterministic and metaheuristic algorithms to minimize electricity cost and reduce peak power demand. Hamed Shakouri and Aliyeh Kazemi was carried out to lower energy cost for householders using the multi-objective mixed integer linear programming and the results verify that the proposed model covering few scenarios worked well to reduce daily energy cost to acceptable level [1]. Fady Y. Melhem et al used the mixed-integer linear programming model for different scenarios with a various grouping of production and consumptions systems to minimize the electricity bills of the residential consumers [2]. Another investigation carried out by B. Lokeshgupta and S. Sivasubramani studied about a multi-objective mixed-integer linear technique with the battery storage system for multiple residential consumers to reduce their electricity bills while as utilities primary goal to reduce their system peak load demand [3]. Veras JM et al introduced a home energy management system that aims to schedule the use of home appliances based on the price of electricity in real-time and on the consumer satisfaction in which the multi-objective optimization model solved using the non-dominated sorted genetic algorithm (GA) [4]. Yi Liu et al developed a satisfaction model for different types of household appliances to minimize the energy expense considering different demand response strategies such as demand-limit-based and injection-limit-based [5]. Nadeem Javaid et al employed binary particle swarm optimization (BPSO) and cuckoo search techniques to reduce the electricity bill and high peaks and made a comparison of the results obtained from using these techniques [6]. A distributed energy management algorithm was designed to optimize the real-time demand of the entire building against abruptly updated rooftop solar generation and real-time price of energy [7]. Boyang Li et al studied cost-effective runtime scheduling designed for the schedulable and nonschedulable appliances to schedule the appliances and rechargeable battery cost-effectively while satisfying users' preferences using the iterative alternative algorithm [8]. George Ifrim et

al proposed a shifting optimization algorithm for a small community of 11 modern houses with 8 photovoltaics and smart appliances that can be remotely controlled via tablets or mobile phones to reduce the electricity bills and peak power loads [9]. Malek Zaibi et al proposed two types of management strategies that are compared in the way they share the hybrid power sources between the storage devices and the electrical and hydraulic loads [10]. Monyeiab and Adewumiab put forward a combined energy management system based on the demands and constraints of consumers such as time of dispatch, cheaper tariff, minimum cost operation, low carbon emission, dynamic pricing [11]. Zhuang Zhao et al were other investigators studying home energy management system by scheduling power consumption in households to reduce electricity bills and improve the peak-to-average ratio [12]. Petra Mesarić and Slavko Krajcar worked on residential demand side management integrated with electric vehicles (EVs) and renewable energy sources using a mixed-integer program in order to schedule optimal power and operation time for EVs and household appliances [13]. Afshin Najafi-Ghalelou et al studied about optimal energy management of interconnected multi-smart apartment buildings considering energy flow among them using the mixed-integer programming [14]. Amir Hossein Sharifi and Pouria Maghouli developed a novel scheduling procedure for power consumption in homes equipped with energy storage devices and claim that their proposed optimal power scheduling method reduced electricity bills and improve peak-to-average ratio while considering of residents' comfortability [15]. Hessam Golmohamadi et al proposed a novel approach to optimize the behaviour of household appliances on the basis of retail electricity price considering the uncertainties of electricity price and wind/solar power using stochastic programming [16].

Unlike previous studies, this study aims to optimize daily operation times of the household electrical appliances and storage devices to minimize both minimum cost and peak load through the stochastic optimization process. Considering the start and stop of electrical household appliances as 1 and 0, the binary-coded genetic algorithm (BCGA) may be more effective compared to other methods such as the mixed integer linear programming etc. The BCGA software was designed for three scenarios and household types to find optimal operation times which help reduce daily operation cost and peak load demand to more economic levels and the results obtained were meaningful and encouraging under certain conditions.

Two are the key factors that mainly distinguish this manuscript from the others where the first is that the proposed GA is useful for both reducing the bill and cutting the peak-load; the second key factor is that the proposed GA is solved via a binary code. The numerical results demonstrate that the combination of GA and binary coding proposed in this paper allows achieving the optimal scheduling faster and more effective and reliable.

# APPLYING GENETIC ALGORITHM TO HEMS

In this section, we will discuss how to apply genetic algorithms to home energy management system.

# System description and proposed method

A typical home energy management system (HEMS) connected to a smart grid is simply shown in Fig. 1. The most vital component in this system is the controller that can monitor and control the household electrical appliances through a WiFi or similar communication networks according to the optimal results found. The main objective in this work is to decrease high power demand in time intervals depending on the tariff, user preferences and the characteristics of electrical household appliances as well as to maintain the energy cost low during the day. In a HEMS, electrical household appliances are assumed to be smart home appliances (SHA) and generally divided into 4 categories according to their operation condition. They are fully time shiftable, partly time shiftable, non-time shiftable and power shiftable. A washing machine, dishwasher, cloth dryer are fully time shiftable appliances (FTSA), the vacuum cleaner, the hair dryer, the toaster partially time shiftable appliances (PTSA), and the refrigerator, indoor and outdoor lighting and air conditioning are referred to as non-time shiftable appliances (NTSA). Power shiftable appliances (PSA) are usually a charging unit of electric vehicles and an electric motor that pumps water into the water tank and their energy levels are unchanged and power levels vary from minimum to maximum. Optimum load distribution with low energy cost and less transmission loss can be determined depending on customer preferences. This is mainly is related to operation hours and duration of each electrical appliance for a day. Accordingly, each household electrical appliance has a rated power as well as start-end times and operation time. In general, ToU tariffs have a variable rate during the day. For larger residential consumers, ToU tariff that a lower energy rate typically applies throughout the night is common and in this investigation ToU tariff is assumed to be employed for electricity pricing.

From this perspective, we assume that residential electricity unit prices are 0.5445, 0.7997 and 0.3405 \$/kWh at the periods from 06.00 to 17.00, 17.00 to 22.00 and 22.00 to 06.00 respectively. Besides, household appliances possessing the above load characteristics as shown in Tables 1 and 2 are considered to be a typical load profile for each home.



Fig. 1. A typical system architecture.

Table 1. A set of typical a	appliances for 1 <sup>st</sup> household.
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Appliance	<b>Operation range (h)</b>	<b>Operation time (min)</b>	Average power (kW)
Fully Time Shiftable			
Dishwasher	1-24	90	1.80
Washing machine	1-24	90	0.80
Clothes dryer	1-24	60	2.50
Partially Time Shiftable			
Iron	18-22	90	1.00
Vacuum cleaner	9-12	90	0.50
Oven	17-20	45	2.00

Hair dryer	6-9	10	2.10
Toaster	6-10	15	1.30
Electric kettle	6-10	15	2.10
TV	8-24	480	0.10
Non-Time Shiftable			
Fridge	1-24	1440	0.15
Indoor lighting	7-8, 19-24	480	0.20
Outdoor lighting	1-7, 19-24	780	0.10
Fully Power Shiftable			
Storage devices	<b>Operation range (h)</b>	Capacity (kWh)	Average power (kW)
Electric vehicle	1-24	10	2.0
Water pump	1-24	0.5	0.3

Table 2. A set of typical appliances for 2<sup>nd</sup> household.

Appliance	<b>Operation range (h)</b>	<b>Operation time (min)</b>	Average power (kW)
Fully Time Shiftable			
Dishwasher	1-24	60	1.50
Washing machine	1-24	60	0.50
Partly Time Shiftable			
Iron	7-21	60	1.00
Vacuum cleaner	9-21	45	0.50
Oven	16-20	30	2.00
Hair dryer	6-8	10	1.80
Toaster	6-9	10	1.30
Electric kettle	6-10	10	2.10
TV	7-24	240	0.10
Non-Time Shiftable			
Fridge	1-24	1440	0.15
Indoor lighting	7-8, 19-24	480	0.20
Outdoor lighting	1-7, 19-24	780	0.10

The flowchart of the GA optimization process is depicted in Fig. 2. The process of the GA is generating an initial population randomly that contains a set of individuals within given constraints in which each individual contains a solution to the problem, calculating the fitness values for each individual, selection, crossover, and mutation. Here, operation times of the electrical household appliances, which are shifted in time and power, are generated by random binary strings and their fitness values are calculated for each binary string. The most fitted individuals are selected using the top-pop size selection method in which the GA sorts the population from the best values to the worst values, and the half-top of best values will be selected based on their fitness value, and the selected individuals are employed to obtain different individuals by means of crossover and inversion mutation operations which are key operators in optimization process by the BCGA for HEMS.



Fig. 2. Flowchart of genetic algorithm optimization.

The proposed algorithm for crossover operation is described below and its implementation is shown in Fig. 3.

- Determine the number of the ones in the strings, *n*.
- Generate a random integer from 1 to *n*-1, *r*.
- Calculate the number of zeros on both the right and left sides of the strings,  $a_{nl}$ ,  $a_{nr}$ ,  $b_{nl}$ ,  $b_{nr}$ . If the maximum number of zeros  $(a_{nm}, b_{nm})$  for each string is less than *n*-*r*, set *n*-*r* to the smaller value or values.
- Copy *n*-*r* ones in string *A* to the side with more zeros in string *B* and delete the extra *n*-*r* ones.
- In the same way, copy *n*-*r* ones in string *B* to the side with more zeros in string *A* and delete the extra *n*-*r* ones.

In order to avoid early convergence, mutation is applied after crossover implementation and for this type of optimization problem inversion mutation is selected as illustrated in Fig. 4. Thus, necessary improvements are made through successive generations. Further, to maintain the best available solution in the genetic process, the best individual is saved in each generation and passed to the next generation. The designed genetic algorithm ends when the maximum number of generations is reached. Furthermore, it is assumed that all the electrical household appliances operate once in a day for the designed software.



Fig. 4. Implementation of the inversion mutation for HEMS.

# **Problem formulation**

The optimization problem of a typical home energy management can be formulated to simultaneously minimize daily energy cost and peak power demand. This is simply a multi objective optimization problem and may be solved by using appropriate computational techniques. It is apparent that meta-heuristic methods may usually find better solutions due to the nature of this problem and the BCGA was used to find possible global optimal solutions to problem under consideration. The optimization process is handled in three scenarios: only daily energy cost minimization, only peak power demand reduction, and both cost minimization and peak power demand reduction. We have two households electrical appliances as given Table 1 and 2 and each appliance has starting-ending times and operation time. The time resolution is assumed to be 5-minute for a more effective computation, that is, a day corresponds to 288 time slots and the shortest time a household appliance operated is 5-minutes. It should be emphasized that it is assumed to be no time delay during the operation of all the household electrical appliances. The above-mentioned problem can be formulated as follows for lower cost and less peak power demand.

$$\operatorname{Min} F_{1} = \sum_{t=1}^{T} \left( \Delta t \times \left( \sum_{a=1}^{A} U_{a}^{t} \times B_{a}^{t} + \sum_{b=1}^{B} X_{b}^{t} \times B_{b}^{t} + \sum_{c=1}^{C} Y_{c}^{t} \times B_{b}^{t} + \sum_{d=1}^{D} Z_{d}^{t} \times B_{d}^{t} \right) \right) \times e(t), \quad (1)$$

where  $T \triangleq \{1, 2, 3, ..., 287, 288\}, \forall t \in T \text{ and } B_a^t, B_b^t, B_c^t \text{ and } B_d^t \in \{0, 1\}.$ 

$$\operatorname{Min} F_{2} = \sum_{i=1}^{n} P_{i}^{t} \leq PPD, \qquad (2)$$
where  $PPD = (\sum_{a=1}^{A} U_{a}^{t} + \sum_{b=1}^{B} X_{b}^{t} + \sum_{a=1}^{C} Y_{a}^{t} + \sum_{d=1}^{D} Z_{d}^{t}), \forall t \in T.$ 

where  $PPD = (\sum_{a=1}^{A} U_{a}^{t} + \sum_{b=1}^{B} X_{b}^{t} + \sum_{c=1}^{C} Y_{c}^{t} + \sum_{d=1}^{D} Z_{d}^{t}), \forall t \in T$ 

 $Min \,\omega_1 F_1 + \omega_2 F_2,$ 

where  $\omega_1$  and  $\omega_2$  are the weight coefficients,  $\omega_1 + \omega_2 = 1$  and  $\omega_1$ ,  $\omega_2 \in [0, 1]$ .

As can be seen here, there are two objective functions that are to be optimized. They can be reduced to a single objective function, thus providing an easier solution. The multi-objective

(3)

optimization problem given by Equations (1) and (2) was solved by the BCGA for each household. Here, operation times of the electrical household appliances, which are shifted in time and power, are generated by random binary strings and their fitness values are calculated for each binary string. The most fitted individuals are selected using the tournament selection and the selected individuals are employed to obtain different individuals by means of crossover and inversion mutation operations which are key operators in optimization process by the BCGA for HEMS.

# **RESULTS AND DISCUSSIONS**

In this section, we describe the simulation results and the discussion of our proposed method, in order to test the validity of the proposed method, the smart grid-connected houses having various household appliances with and without the storage devices. The 1<sup>st</sup> household has smart electrical appliances with two storage devices that are an electric vehicle and a water pump. The 2<sup>nd</sup> household has also smart electrical appliances without storage devices. There are two different types of families living in these households therefore operation, starting and ending times of electrical appliances in the households were considered to be different from each other. We assumed that each electrical appliance has a fixed operation times which are multiples of 5 minute such as 90 and 10 minutes for washing machine and hair dryer respectively. We know that a washing machine can be less or more operation time in daily life depending on washing program so that there may be an error associated with cost and power calculations. However, this error can be ignored since it has no major effect on the application of the proposed method to the problem under consideration. Cost and power calculations were made based on three scenarios such as only cost, only power and cost and power in the households.

The proposed method is performed using MATLAB to solve the BCGA optimization problem. The parameters used for GA, number of generations G = 100, the population size of each generation N = 100, the probability of crossover  $P_c = 0.9$ , and the probability of mutation  $P_m = 0.03$ . As mentioned above, we proposed a weighted-sum method that combines multobjective functions into a single objective function which can represent all scenarios, in the only cost reduction scenario  $w_1 = 1, w_2 = 0$ , in the only power reduction scenario  $w_1 = 0, w_2 = 1$ , and in the cost-power reduction scenario  $w_1 = 0.5, w_2 = 0.5$ .

Fig. 5 shows the daily power consumption results for optimal operations of household appliances in the two households for three scenarios. The total power consumption results in the two households are 29.15 kW and 12.14 kW respectively. According to scenario 1, which is based only on reducing daily energy costs, the power consumption reached the highest values in the two households 4.78 kW and 2.13 kW within 1-5 time slots respectively, in which the cost of electricity is the cheapest. Unlike scenario 1, scenario 2 is based on directly reducing peak power level rather than cost. In this scenario, power consumption reached the highest values in the two households 2.15 kW within 11-14 time slots and 0.9 kW within 16-17 time slots respectively and thus changes mostly occurred during the day and evening times when the electricity price is higher. As in scenario 3, when both power consumption and cost reduced, power consumption was highest in the two households at 2.25 kW and 1 kW within 1-5 time slots respectively when the electricity price is lower. The power consumption in the third scenario was smoother than the others as seen in Fig. 5. Table 3 shows the variation of power consumption, average cost, and total cost in the two households for the three scenarios. From the results, it seems that the proposed approach method worked well to reduce power consumption and cost during the day.



Fig. 5. Variation of power consumption in the two household for the three scenarios.

Table 3. The variation of power consumptions, average cost, and total cost in the two households for the three scenarios.

		Household 1			Household 2	
Scenario	Variation of	Average	Total cost (\$)	Variation of	Average	Total cost
	power (kW)	cost (\$)	Total Cost (\$)	power (kW)	cost (\$)	(\$)
1	0.15-4.78	0.53	12.62	0.15-2.13	0.25	6.06
2	0.22-2.15	0.67	15.97	0.15-0.9	0.28	6.81
3	0.15-2.25	0.58	13.84	0.15-1	0.25	6.11

Fig. 6, Fig. 7, and Fig. 8 show variations of daily power consumption and costs for the clothes dryer, TV and electric vehicle charging unit in household 1 according to all three scenarios respectively.

The clothes dryer is a fully-time shiftable appliance and the operation range between 1-24 time slot and operation time 60 minutes according to Table 1. From the perspective of the first scenario, Fig. 8 shows the clothes dryer worked during the hours when electricity prices are cheap within 2-3 time slots, while the power consumption increases during these hours as expected. When a similar load is analysed from the perspective of the second scenario, it is seen that the largest power consumption occurs during the evening, when the electricity prices are the highest. In the case of the third scenario, the power consumption is spread as equally as possible. The daily cost for this electrical appliance was found to be \$0.85, \$2 and \$1.36 for each of the three scenarios respectively.





The TV operated with a partial time shift is examined for the three scenarios, it is seen from Fig. 7 that the change in power consumption is very limited; such that, in the first and third scenarios, the power consumption was 0.1 kW within 8-16 time slots when the electricity price is lower as expected, while in the second scenario, the power consumption varied during evening and night times when the power consumption is the lowest from 0.067 kW in the 16<sup>th</sup> time slot to 0.1 kW within 17-23 time slots then decreased to 0.033 kW in the 24<sup>th</sup> time slot. The daily cost is the same for the first and third scenarios \$0.44 while the daily cost was highest in the second scenario \$0.52.



Fig. 7. Comparison of cost and power in TV for the three scenarios.

The electric vehicle charging unit, seen as a power shifting load, was examined for all three scenarios. Since the first scenario is based on minimizing cost, power consumption is highly increased between 1-5 time slots when electricity is cheaper. In the second scenario, power consumption increased during the daytime when the electricity price more expensive, unlike the first scenario. According to the third scenario, the power consumption is the same of the first scenario to make a balance between the cost and power. Under this load condition, the daily energy cost was \$3.41, \$5.45 and \$3.41 in all three scenarios, respectively. It appears that simultaneous optimization of cost and power consumption provides an important advantage in balancing the daily cost and power consumption in home energy management systems.



Fig. 8. Comparison of cost and power in electric vehicle charge unit for the three scenarios.

# CONCLUSION

The proposed method is capable of solving the multi-objective constrained optimization problems under consideration to reduce both daily energy cost and peak power demand under various cases because the BCGA perfectly adapts itself to the nature of on/off control household appliances in certain operation times. It is verified that the proper optimization of operation times is highly crucial in a HEMS including few constraints, fully time shiftable, partially time shiftable, non-time shiftable and power shiftable household appliances. It is also verified that the power storage devices play a major role in reducing the cost for HEMS. Small-time resolution is highly influential on the optimization process through the BCGA since it creates more ones in the strings in a population for proper crossover and mutation operations. It may be said that the convergence time is short in this optimization process and the real-time control of the household appliances may be possible in case of sudden changes of consumer preferences. It can be concluded from the results, the advantages, and the efficiency of using HEMSs in residential homes by reducing both daily cost and peak power and the benefits for utility companies by reducing the peak power demand which leads to increase capacity, efficiency, and reliability in the distribution network.

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# REVIEW OF THE POWER SYSTEM RELIABILITY ASSESSMENT METHODOLOGIES

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#### ABSTRACT

The main function of the power system is to meet the demand for system load or consumption in the most reliable and cost-effective possible way, while ensuring the continuity of services and the quality of electricity. In order to achieve the required level of reliability, energy system managers, designers, planners and operators use different methodologies and use different criteria/indices.

The aim of this paper is to provide more detailed information on the main approaches to reliability of the power system, more specifically of the transmission system, to present their advantages and disadvantages, and to assess when the approaches are applied. Assessing the overall reliability of a power system is a very complex task. The large number of elements and the different possible operating modes make the calculations practically impossible. This paper presents how a power system can be decomposed. Some of the methods allow to assess the impact of individual components on the reliability of the system or the consequences of a particular failure on the system. System-level assessment methodologies are also used, but these are more associated with long time processes. It should be noted that deterministic or probabilistic methods are generally used. Each of these has advantages, but there is an increasing emphasis on the latter. Although there are many approaches to power system reliability, they can be broadly divided into large-scale and slow computational approaches or smaller-scale and fast computational approaches. Depending on the desired result, one or the other method is chosen accordingly.

Keywords: power system, evaluation methods, reliability indices

# **INTRODUCTION**

Electric power system is one of the largest and the most complex systems established by the mankind. It consists of uncounted number of facilities and structures, systems and subsystems, components and equipment, and the complex interactions among all those [1]. With electric power system becoming more and more complex and intelligent these days, its uncertainty also increases. This brings new challenges to reliability assessment and management of the power system. The reliability assessment of power system has been developed for nearly half a century, from deterministic methods to probabilistic methods, from local to wide area, from simple to complex research methods.

# RELIABILITY

Reliability to different people means different things. The term reliability can be related to certain product quality or resistance to certain operating conditions. The generally accepted definition of reliability defines the reliability as the characteristic of an item expressed by the probability that it will perform a required function under stated conditions for a stated period of time [1].

$$R(t) = P[C \text{ did not fail in time interval } [0, t]], \tag{1}$$

where C – component; R – reliability; P – probability; t – time.

The mathematical definition of reliability is related to the probability density function f(t) witch is part of probability theory. Reliability R(t) is the probability that the variable is at least as large as *t*. For continuous random variable, the related equation is the following:

$$R(t) = \int_{t}^{\infty} f(t)dt.$$
 (2)

For discrete random variable, the related equation is the following:

$$R(t_i) = \sum_{i=1}^{\kappa} f(t_i).$$
 (3)

The term reliability is divided into two terms when dealing with the power systems [2]. Those two terms are adequacy and security. The adequacy is related to the existence of sufficient generation of the electric power system to satisfy the consumer demand. The security is related to the ability of the electric power system to respond to transients and disturbances that occur in the system [1].

#### **Adequacy and Security**

As mentioned earlier, reliability in the context of a power system, is divided into the two aspects of adequacy and security, as shown in Fig. 1.



Fig. 1. Subdivision of system reliability

System adequacy relates to the existence of sufficient facilities within the system to satisfy the consumer load demand or system operational constraints. These include the facilities necessary to generate sufficient energy and the associated transmission and distribution facilities required to transport the energy to the actual consumer load points [2]. System security relates to the ability of the system to respond to disturbances arising within that system. Security is therefore associated with the response of the system to whatever perturbations it is subject to. These include the conditions associated with both local and widespread disturbances and the loss of major generation and / or transmission facilities, which can cause dynamic, transient, or voltage instability of a power system [2]. System adequacy is associated with static conditions, which are long-term analyses. On the contrary, system security is associated with dynamic or transient conditions and associated with short-term analyses.

# Power system hierarchical level

An overall power system can be divided into the three basic functional zones of generation, transmission, and distribution, and be organized into the three hierarchical levels (HL) shown in Fig. 2. Hierarchical Level I (HLI) involves only the generation facilities. Hierarchical Level

II (HLII) involves both the generation and transmission facilities. Hierarchical Level III (HLIII) involves all three functional zones [3].



Fig. 2. Hierarchical level [2]

The analysis of the reliability of the first hierarchical level (HL I) is commonly referred to as the capacity adequacy assessment and includes the generation capacity needed to meet the future needs of the system. This level shall also include the calculation of the additional generation reserve of the electrical system or corrective actions of the necessary generation facilities related to the balancing services of the system. Often, the model includes a generation station that has individual generation units and a load. The entire substation/station or individual items are modelled, depending on the target you have asked. Modelling is also possible for generation stations or individual systems connected, but only for generation stations/systems and lines that connect to another generation point and the electricity transmission network excludes analysis.

The second hierarchical level (HL II) reliability analysis is often referred to as an assessment of a complex system or bulk electrical system and includes an integrated generation and transmission system. The reliability assessment at this level focuses on the ability of the system to transmit electricity from the generation site (HL I) to the main load points. Suitability assessment HL II includes load flow analysis, contingency analysis, generation planning, transmission congestion reduction and optimum mode selection. The overall assessment of the reliability of the production and transmission system may include many tasks and requirements that extend the model and make it much more complex.

The third hierarchical level (HL III) covers the entire electricity system, including the distribution system and its equipment. This level shall assess the amount of electricity required to ensure each load point. Although it is theoretically possible to analyse the whole electrical system, due to its complexity, the reliability analysis is not carried out in practice. It is accepted that this hierarchical level typically involves an analysis of the reliability of the distribution system. The main function of the distribution system is to distribute electricity, which is traditionally transmitted from transmission over the network. As the number of redistribution points and individual customers is very high, it is natural that certain problems arise as regards voltage levels, harmonic levels and other parameters of power quality.

#### **Reliability approaches**

In this paper we will focus on main analytical approaches and Monte Carlo simulation approach as well. The vast majority of techniques have been analytically based and simulation techniques have taken a minor role in specialized applications. The main reason for this is because simulation generally requires large amounts of computing time, and analytical models and techniques have been sufficient to provide planners and designers with the results needed to make objective decisions. [2].

Analytical techniques represent the system by a mathematical model and evaluate the reliability indices from this model using direct numerical solutions. They generally provide expectation indices in a relatively short computing time. Unfortunately, assumptions are frequently required in order to simplify the problem and produce an analytical model of the system. This is particularly the case when complex systems and complex operating procedures have to be modelled. The resulting analysis can therefore lose some or much of its significance. The use of simulation techniques is very important in the reliability evaluation of such situations.

Simulation methods estimate the reliability indices by simulating the actual process and random behaviour of the system. The method therefore treats the problem as a series of real experiments. The techniques can theoretically take into account virtually all aspects and contingencies inherent in the planning, design, and operation of a power system. These include random events such as outages and repairs of elements represented by general probability distributions, dependent events and component behaviour, queuing of failed components, load variations, variation of energy input such as that occurring in hydrogeneration, as well as all different types of operating policies [2].

### **Reliability indices**

Next part of reliability assessment is indices. There are many possible reliability indices, which often are interdependent. Depending on the application, a suitable set of indices has to be chosen, to perform the reliability evaluation.

For the analysis of complicated systems like electric power systems, more sophisticated indices have to be used. This is due to the fact, that an electric power system does not only have two possible states, but an enormous variety of partially failed states, where a part of the load is lost. A good way to address this is to use the indices named annual energy not supplied (ENS), also called loss of energy expectation (LOEE), or the annual power not supplied (PNS), also called loss of load expectation (LOLE). These indices are based on the concept that power is either supplied or not. Power quality issues, which are not treated in this paper, cannot be described with those indices. If interruption cost (or reliability worth) should also be taken into account, indices like the cost of energy not supplied (CENS) and the cost of power not supplied (CPNS) can be used [4].

### POWER SYSTEM RELIABILITY ASSESSMENT METHODS

As it is known, power system reliability modelling techniques have evolved from traditional deterministic modelling methods to the current more advanced probabilistic modelling methods. As power systems grow much larger and more complex, the need for the rigorous analysis of bulk power system reliability becomes more obvious. Because of the stochastic nature of system behaviour, such as component outages or load-level changes, the development and application of probabilistic techniques for modelling the bulk power system and evaluating an appropriate set of expected risk indices have received considerable attention [5]. In the probabilistic modelling method, uncertainties affecting power system reliability are

represent component states, electric load levels, system states, etc. Such a probabilistic modelling method enables the calculation of probability, frequency, and duration indices of system failures. These indices are no longer deterministic values but expected values of probability distributions [5]. Probability methods can be divided into analytical or simulation methods.

The most common methods for reliability assessment are:

- Contingency enumeration method
- Minimum cut/tie set method
- Event tree method
- Fault tree method
- Monte Carlo simulation method

The following will provide a brief overview of all the above methods.

# **Contingency enumeration method**

The contingency enumeration method (sometimes called the state enumeration method) is analytical method, which, as the name implies, assesses the reliability through analysis of a selected number of contingencies [4]. For composite system reliability evaluation, the contingency enumeration method can be structured in four steps, see Figure 3.



Fig. 3. Structure of the contingency enumeration method [5]

The first step starts with the structure analysis of the simulated system. This includes: power system reliable boundaries, system operating mode scenarios, load flow method (AC or DC), modelling detail level, etc. The next phase selects contingencies that should be taken into account in the analysis. In most cases, considering all possible contingencies is unrealistic due to the long computational time, which means the importance of the selection procedure. The goal of contingency selection techniques is to determine from the set of all possible contingencies the subset that will cause system failure. No contingency selection method can attain this goal perfectly; they can perhaps at best provide a subset that contains most contingencies causing system failure. [6] The contingency selection has to be done carefully, because every disregarded contingency adds to the inaccuracy of the evaluation. An easy manner to perform the selection is to regard all contingencies up to a specified order. Single component failures often have little impact on the system and therefore on the reliability

indices. Failure of multiple independent components at the same time is not very likely and does therefore often not contribute significantly to the indices, even though the impact of such a situation is large. Common mode outages, where a single event leads to failure of multiple components, are therefore generally important to identify. The failure of a substation connecting several generators or a tower carrying several power lines can significantly degrade the power system reliability [4]. In the next step, load flow calculations or a performance index (PI) can be used. It is possible to rank contingencies by first solving each contingency using DC or AC load flow, but it would be very time consuming.

$$PI = \sum_{\ell} W_{\ell} \left(\frac{P_{\ell}}{\overline{P_{\ell}}}\right)^n, \tag{4}$$

where:

 $W_{\ell}$  = weighting factor for circuit  $\ell$ ;  $P_{\ell}$  = real power flow on circuit  $\ell$ ;  $\overline{P}_{\ell}$  = power rating on circuit  $\ell$ ; n = an even integer, generally 2.

After contingency selection by performance index it is necessary to evaluate which load flow calculation model to use. Load flow calculations may be either of AC or DC type, where an AC load flow calculation often is necessary to identify the most relevant network problems. In case of an extensive contingency list, for a huge power system, an approach with AC load flow might be unrealistic; instead DC load flow techniques can be used. Utilization of DC load flow will degrade the quality of the entire evaluation, since voltage problems no longer can be identified. A possible compromise is to run DC load flow calculation for all contingencies, to identify the critical ones, which afterwards are calculated again using AC load flow [4]. More about difference of DC and AC power flow approaches to assess reliability and contingencies of power system can find in reference [7].

Some of the identified system problems might be repairable with corrective actions, such as generation rescheduling. Those minor problems will therefore not have impact on the reliability indices. If the system problems cannot be solved with regular corrective actions, evasive corrective actions like load shedding have to take place. Such actions do influence the reliability indices. The applied load shedding strategy is highly relevant for the results for each load point, since a systems wide power deficit could theoretically be solved by load shedding at any load point. Contingencies leading to local problems are less sensitive to the chosen load shedding strategy. In the last step, the predefined reliability indices are calculated (typically on both load point level and system level) and the annualized indices are summed up from all the studied operational states and contingencies [4].

### Minimum cut set method

Another analytical model is designed to evaluate more a specific point in the system is minimal cut set method. This method is quite simple because block diagrams are used. Reliability block diagram is a graphical way to show the relationship between the functioning of the system and the functioning of its components. In practice, a system is often represented as a reliability block diagram in network structure in which the components are connected either in series, parallel, mesh or a combination of them. The cut/tie methods can be used to assess their reliabilities [8]. The minimal cut set method is a good tool to utilize when assessing the reliability of specific load points in the power system. The method reduces computation time by focusing on the system contingencies which are relevant for the selected load points and not for the entire system. The minimum cut set method is sometimes called the failure mode method; since the cut sets define the failure modes of a load point. A minimum cut set is defined as a set of system components which, if all are in failed state, causes outage at a selected load point [4].

The minimal cut sets of the system shown in Fig. 4 a) are (AB), (CD), (ADE) and (BCE), which gives the reliability diagram of Figure 4 b). If the *i*-th cut is named as  $C_i$  and the probability of failure of all the components in  $C_i$  is represented by  $Pr(C_i)$ , then the reliability is [11]:

$$R_{S} = 1 - Pr\left(\bigcup_{i=1}^{n} C_{i}\right) \tag{5}$$



Fig. 4. a) Reliability block diagram in network structure, b) Minimal cut set diagram [10]

#### **Event tree method**

Event tree analysis is the technique used to define potential accident sequences associated with a particular initiating event or set of initiating events. The event tree model describes the logical connection between the potential successes and failures of defined safety systems or safety functions as they respond to the initiating event and the sequence of events [1].

The method may be used either for systems where all components are continuously operational or for systems where some or all components are in standby mode, which includes the logic and switching of sequential operation. Lastly type of system is generally associated with security-oriented systems. In practice, the event tree approach is mainly applied to safety-oriented systems, as other methods mentioned in the paper are more suitable for continuous systems. The application of the method to both types of systems is similar, but there are two certain differences between them.

First, events that may occur with continuously operated systems, or rather components that may fail, can be assessed in any random order. In the case of stand-by systems or any system in which the performance of a particular component depends on the failure of another component, the sequence of events shall be considered chronologically.

The second difference is the starting point of the event tree [9]. In the case of continuous systems, the reference point is the normal system and the event tree is counted as a sequence of events related to the success and failure of system components. In the case of standby systems and, in particular, safety and mission-oriented systems, the event tree shall be used to determine the various possible outcomes of the system after a given initial event, which is usually an undesirable event or situation.

# Fault tree method

This method is used for the reliability analysis of complex systems and based on the event that will lead to system failure. The fault tree analysis is an analytical technique, where an undesired state of the system is specified and then the system is analysed in the context of its environment and operation to find all realistic ways in which the undesired event can occur [10].

First of all, the fault tree method was developed as a means of qualitatively assessing fault processes in complex systems and determining the consequences of failure on the system. And that is one of the most important advantages of this method. However, it can also be used to carry out a quantitative assessment. This method takes into account a specific fault condition called a top event and creates a tree that identifies the various combinations and sequences of other failures that are considered to be a fault. The method is relatively simple, with a certain condition of failure or failure, which is considered to be a major event [11]. A fault tree is further constructed to identify other failures or combinations that lead to the occurrence of the underlying event. The process starts with a specific system failure mode. The causes of this system failure are progressively divided into an increasing number of hierarchical levels until a level is reached at which the malfunction or effects of the main components of the system can be determined.

This method is often used as a qualitative evaluation method to help designers or operators decide how the system or subsystem may fail due to the operation of individual components and what measures can be used to correct the causes of the failure. The method can also be used for quantitative evaluation, in which case the reliability data of individual components are inserted into the tree at the lowest hierarchical level and combined using the logic/structure of the tree to assess the reliability of the entire system under investigation.

The fault tree analysis procedure steps together with their main mutual relationships are shown in Fig. 5.



Fig. 5. Fault tree procedure steps

#### Monte Carlo simulation method

Monte Carlo simulation involves the analysis of repeated samples or trials created using random numbers. Monte Carlo methods have been used widely in analysing complex mathematical problems, stochastic processes, medical applications, engineering systems, and reliability evaluation [12].

In the application of reliability, the simulation process essentially attempts to simulate the actual components of the system and develop patterns of system behaviour, including the random nature of interconnected processes. During the process, the number of failures, time between failures, recovery time, etc. can be estimated. Mathematically plausible or long-term mean values can be obtained and, if necessary, the probability and frequency distribution of each variable can be obtained. The stochastic process is facilitated by the generation of random numbers, which are then converted into density functions describing the behaviour of components and variables of the system in question. Random numbers and density functions generated form an important and essential part of Monte Carlo's modelling.

It is important to appreciate that most of the probabilistic techniques presently available for reliability evaluation are in the domain of adequacy assessment [13]. There are two main approaches to assessing the adequacy of complex systems using the Monte Carlo methods. These methods are commonly referred to as sequential and non-sequentional procedures. For non-sequentional technique, the status of all components is taken and the resulting system states are not evaluated chronologically. Non-sequentional non-sequential techniques simulate the upward and downward state of all components to obtain system performance. The resulting system condition is assessed by combining all component states according to the chronological model from which the required reliability indicators are derived.

# CONCLUSION

In this paper we discuss the concept of reliability in the electrical system, how reliability can be assessed through adequacy or security, thus providing methods for assessing reliability. The short familiarized hierarchy of the electrical system and parts of the system form each level. This is important because it partly determines the choice of methods. The reliability indices used at HL1 and/or HL2 system levels are briefly mentioned. Assessing the overall reliability of the electrical system is a complex and practically impossible task because it is constantly changing, there is no single steady state. The reliability methods outlined in this paper relate to the long-term reliability assessment or also to the so-called static state of the system. At HL2 level, it is accepted that the assessment is the adequacy of the system and that the methods are generally probable, which are divided into analytical and simulation. Analytical models such as fault tree or event tree are generally used to assess parts of systems. This can be a particular load point or part of the electrical network segment, such as substation bus. Assessing the entire power system would be difficult, as even modelling that one element of the system could be a two-state full model would be practically infinite. Enumeration method or Monte Carlo simulation method is more appropriate for the evaluation of the whole system. They are different but can be used to measure the reliability of the system fairly well. The security assessment in this paper is virtually intact because it uses methods that evaluate physical processes during a failure and how the electrical system withstands faults/failures. These are transient, dynamic processes, which are usually classified as short-term phenomena, and specific programs are used to assess them. A deterministic method of reliability is often used for security assessment and will be further reviewed in the future.

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# APPLICATION OF MULTI-PERIOD OPTIMAL POWER FLOW METHOD FOR CRITICAL NETWORK NODES IDENTIFICATION

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#### EXTENDED ABSTRACT

#### **OVERVIEW**

Modern technology and lifestyle have made electricity one of the main needs of society. Several studies [1-3] have identified a linear relationship between electricity consumption and economic growth. It is probably not difficult to realize that a reliable and secure supply of electricity is indispensable to ensure the needs of the households, further technological development, industrial progress, the smooth operation of facilities, and economic growth [4].

The identification of critical elements affects the whole system and, of course, the security of this system. In an ideal world, all network elements should be protected [5]. However, in the real world, this is usually not possible, as there is a shortage of various resources and an attempt is made to find the most optimal solution.

Therefore, this paper presents the application of optimization methodology for critical network nodes identification. This identification could help to rank the most critical elements and make appropriate decisions for their additional protection.

#### **METHODS**

#### **Optimization problem and constraints**

Analysis of the optimal power flow (OPF) problem in this paper ensures that consumers are supplied with electricity at the lowest possible generation cost. The power output of generating units as well as the network variables (voltage magnitudes and angles) are determined in OPF to minimize total operating costs [6].

The objective function consists of the costs incurred in generating energy and not delivering a certain amount of generation in relation to the demand. The formulation of the optimization function is given below:

$$OF = \sum_{g,t} C_g p_{g,t}^G + \sum_{d,t} \text{VOLL } p_{d,t}^{shed}, \tag{1}$$

where  $C_g$  – generating unit g production cost (\$/MWh), VOLL - the value of loss of load (\$/MWh),  $p_{g,t}^G$  – is production level (MW) of generator g at hour t,  $p_{d,t}^{shed}$  - load shedding in demand d at hour t (MW). The equality constraints of the problem describe the balance of power at network nodes. Accordingly, the inequality constraints are linked to certain safety limits and the power flow of the lines cannot be higher than expected, the capacity of the generators must meet the specified maximum and minimum values, and their ability to change the power must not exceed the specified limits.

The basic principle of the model is that it must operate in a cycle. This means that at the beginning the model is formed and the necessary data is provided. Using the obtained data, the model solves the nonlinear programming optimization problem and records the obtained answer. The system is then reset to the original set state, the necessary change is made, and a new result is obtained. This is repeated until the required number of cycles, which is equal to the number of lines in the network, is reached.

#### **REFERENCE SYSTEM**

The IEEE 24-bus system was chosen to test the developed algorithm. Fig. 1 shows a graphical representation of this system. The data required for this system can be found in [6].



Fig. 1. Diagram of the reference power system

The system has three wind generators at nodes 8, 19, and 21 with capacities of 100 MW, 150 MW, and 200 MW, respectively.

#### RESULTS

In this work, the N-1 scenario was analysed. This scenario includes all cases where any one of the lines in the system can be disconnected. In the real world, these cases can be caused by a variety of causes: natural disasters, equipment failures, or specially caused damage (malicious event).

The effect of branch disconnection on certain network nodes indicates that the greatest impact is made on Node 4, where a 733.7 MW load is disconnected due to the failure of the 2.6 branch. Looking at the extent to which the inactivity of the various branches affects load and consumption, it can be seen that in total, 1041.4 MW of energy is not supplied. High load shedding volumes are also monitored in Node 3. Here, 565.1 MW is lost due to the failure of branch 3.24 and 363.2 MW due to the failure of branch 15.24. Also, although the load losses at Node 2 are relatively small compared to the values mentioned above, 19 of the 34 branches have an impact here, so this also implies that additional safety measures should be taken.

The accuracy and at the same time uncertainty of the proposed method is highly dependent on the input data. In reality, data for the time period when energy consumption is highest could be used, as this would be in line with the worst-case scenario and when is the most important time to ensure safety of energy supply.

#### CONCLUSIONS

The OPF method was applied for power system safety analysis because the solution indicates if there is sufficient available capacity to feed all the loads. The results of the reference power system analysis show that the power system is not always resistant to the N-1 contingencies. It should be mentioned that the analysis was performed using a standard system, but the adaptation of a larger system on a country or regional scale should provide more insights into the application of this model.

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# INCREASING EFFICIENCY OF COOL GENERATION ON A DEMAND SIDE SUPPORTED WITH LOWER DISTRICT HEATING NETWORK SUPPLY TEMPERATURE IN A SUMMER MODE

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#### ABSTRACT

Future district heating (DH) systems (so called 4th generation district heating (4GDH) systems) have to work involving (de)centralized renewable heat sources and storage, low network temperatures and both cooling and heating services. The aim of this study is to predict the behaviour of local cooling facilities and possible outcomes. In each case, the scenario and temperature interval are analysed with regard to the energy effect of the replacement of the conventional split system. Two scenarios are simulated for temperature intervals of 50 and 60°C. Assuming domestic hot water (DHW) load, the summer level is only about 80% of the current temperature. This means that the lowest temperature of 50°C may be achieved through temporary manipulation. Based on the temperature needs of the DHW systems only, the results of this survey show that the supply temperature in the network may be lowered to 50°C, consistent with 4GDH concept, for more than half of the summer. Depending on the configuration, the resulting savings are between 16% and 24%. The impact of some crucial parameters, such as the network supply temperature and outdoor one, on the energy performance of the distributed cool generation are studied. The results obtained indicated that the cooling demand is not met (52% of the reference value) after any year of implementation, due to the fact that outdoor temperature is expected to increase. From the aspect of traditional DH networks, capacity of additional cooling installations is much lower than the required value under the design conditions. Summer operational regime is eligible for current climate conditions, which improve feasibility of the entire system during the year.

Keywords: 4th generation district heating, energy, outdoor, load

# **INTRODUCTION**

Novel district heating (DH) system designs are all about a rule of low temperature heat supply, recently supported by renewable and waste heat options [1]. Ability to use waste energy sources is helpful in the process of decarbonizing the heat supply industry [2], and results to the need of low DH network supply temperatures. Future DH systems (so called 4th Generation District Heating (4GDH) systems) have to address issues such as integration of (de)centralized renewable heat sources and storage, low network temperatures and high fluctuation of the supply temperature [3]. In [4], different configurations of a DH system have been considered, varying the volumes and the water flow rates of the thermal energy storages (TESs). In [5], a number of TES configurations including use of building envelope are compared. Wang et al.

[6] indicate that the high supply temperature is worse in terms of ensuring hydraulic stability at a substation than the low one. On the other hand, this newest generation is characterized by higher supply temperatures in case of a district cooling system [7]. Paper [8] surveys supply temperatures in multi-story residential houses in Gothenburg, Sweden.

DH network is often deep buried and as a matter of fact installing new equipment thus employing externally based leak locating methods such as acoustic ones [9] is complicated. Valincius et al. [10] presented a potential of leak detection by means of data from the pressure gauges installed in a DH network. Mass flow rate and supply temperature are imposed as a boundary condition in the model developed by Guelpa [11]. In research [12], authors focus solely on describing regime when the mass/velocity flows run constant.

Geysen et al. [13] make an analysis of the hourly heat demand based on the average and 90% confidence interval with regards to the day of the week. Idea presented by Tunzi et al. [14] is to verify the theoretical operation range of the space heating (SH) system at different heat demands, from zero thermal load to design conditions. Local heat producing units may generate around 30% of total energy demand [15]. Heating demand control problem is addressed in [5]. The result is based upon detailed engineering calculations that had been conducted individually for each of substations (consumers), considering construction, insulation and its needs in steady-state operation [16]. The methodology in [17] is applied to the decrease of the heat load request happening in the morning in order to minimize the total primary energy consumption. However, papers in which data on energy demands and supply temperatures are gathered tend to not include any observation on the temperatures in summer. Traditionally heating and cooling systems were separated from each other, so only extremes for the cold period of the year were analysed and taken into account by researchers. Merging both requires analysis of warm period on the year extremes. Romanchenko et al. [18] cover modelling during a summer season although electricity generation is primarily considered. Primary energy consumption, greenhouse gas (GHG) emission, and capital costs are used as key indicators in [19]. GHGs are typically carbon dioxide, methane, ozone, nitrous oxide, chlorofluorocarbons, water vapor, etc., which are emitted in different industrial processes. However, only 5 first of them are considered as extremely harmful. The focus in [20] is to evaluate the ratio between the DH load distribution and heat production from solar thermal collectors. The production rate does not always cover the demand rate since solar collectors have the best output during the warm-weather months, when domestic hot water (DHW) heat demand prevails. It is apparent that considerable energysaving effect and GHG emission reduction benefits at the city scale are accessible only by the implementation of energy-conservating measures on consumer side, demand-side structure enhancement, solar energy utilization and efficient technologies such as combined cold-, heatand-power plant (CCHP) on supply side.

Such a system may meet the power demand, and the recovered heat can ensure the heating and cooling loads via the heat exchanger and absorption chiller, respectively. Wu et al. [21] present a nonlinear model for a neighbourhood-scale distributed energy system considering power generation, heating and cooling aspects. A lot of information about cooling systems is listed in [22]. Zarin Pass et al. [23] calculate the combined hourly heating, cooling, and DHW load profiles for several combinations of building sorts in the USA cities.

Both reliability and availability indicators present ladder growths as outdoor temperature rising, i.e., dynamically dependent on outdoor temperature [24]. After determining fault components, state probabilities under various outdoor temperature can be calculated [25].

Some sophisticated simulation simulations and software tools are supportive to calculate the hydraulic and thermal efficiency of the existing system or design a new one [26]. The primary factor for appearance of sophisticated DH systems is many hours of differences in marginal heat supply costs between close and early isolated ones [27]. To assess a performance of a district energy system comprehensively, thorough simulation models tend to be indispensable [9,28–30]. Simpler engineering equation solver software (EES32) with built-in tabulated thermodynamic properties of several working fluids is used to process the simulations in [31]. The technique in [32] has a goal to provide data on system operational patterns and cost-effective quantification with sustainable design of a whole DH system. The goal of this research is to forecast the behaviour of local cooling facilities and possible benefits.

### **MATERIALS&METHODS**

Eq. 1 was used to derive the space heating power demand for each outdoor temperature:

$$Q = G\rho c(\tau_1 - \tau_2), \qquad (1)$$

where G is the desired flow rate according to covered heat load; Q is the heat load of a DH plant which typically depends on time; c is the specific heat capacity of water,  $\tau_1$ , and  $\tau_2$  are design supply and return temperatures, respectively.

The criterion of this study established in [21] indicates the primary energy saving (PES) ratio of the system compatible with the idea described below (lower supply temperature, LST) compared with the conventional (con) separated energy system:

$$PES = \frac{E_{con} - E_{LST}}{E_{con}} \cdot 100\% .$$
<sup>(2)</sup>

Thus, an outdoor temperature-dependent heat demand profile was plotted for each option. As considering that some inputs, such as water density and viscosity, depend on temperature variation, the hydraulic and thermal calculations have to be performed in an iterative way. Fortunately, the water density and viscosity do not vary significantly at the range of normal DH network temperature [28]. For the models where the wind infiltration, solar radiation or thermal inertia of the buildings is used refer to other works, for instance [33].



Fig. 1. Flow diagram of the suggested energy system. (1) steam turbine; (2) heat exchanger; (3) DH network pump; (4) conventional radiator; (5) backup heater; (6) chiller, (7) supportive low-temperature radiator; (8), and (9) supply and return lines, respectively; (10) mixing valve

In each case, the scenario and temperature interval is analysed with regard to the energy effect of the replacement of the conventional split system. Two scenarios are modelled for temperature intervals of 50 and 60°C. ZuluThermo© (8.0.0.7539, Politerm, LLC, St. Petersburg, Russia) was a simulation program built into the GIS Zulu© primarily for DH systems, which was used to simulate two-mode (district heating and cooling) network.

Moreover, instead of the conventional energy system with a compression chiller to supply the cooling demand, here the absorption chiller is available to utilize the recovered heat as the first option. As before [22], equipment for cooling sub-systems may be selected according to the peak value of the design heat demand and the 80% simultaneity usage coefficient. Because the buildings are set to not be cooled when outdoor temperature is below 20°C, the DH network temperature may be as low as 50°C. The second option set temperature of the indoor air that depends on the outdoor temperature. For simplicity, indoor temperatures are set the same for all buildings at 19.5 and 20.5°C as in [5,34]. Then, a model for a SH heat exchanger is applied to evaluate the flow rate extracted from the DH network, by which the DHW temperature after the heat exchanger meets the set temperature. The temperature in a local cooling conduit is determined by means of a heating curve with a summer set point of 60°C. This actual temperature is maintained by adjusting the flow rate of the DH water with the DH valve. With this option, utilization of more generation processes becomes accessible.

Microsoft Office Excel is a universal spreadsheet programme based on the Visual Basic for Applications which is an implementation of Microsoft's event-driven programming language Visual Basic 6. In Excel, it is possible to visualize several technical parameters, temperatures and pressures.

Since the novelty is i) idea, ii) its application, and iii) use of combined actual and simulated data, the equations used in the modelling are known. However, to detail the model some of them are shown below.

Reynolds number is:

$$Re = \frac{\rho v D_i}{\mu},\tag{3}$$

where  $\rho$  is the density (kg/m3), v the fluid velocity [m/s],  $D_i$  was the inner pipe diameter [m],

 $\mu$  was the fluid viscosity (Pas).

The fluid velocity was calculated in the ZuluThermo© simulation for each section of a DH network according to:

$$he = \frac{v^2}{2g},\tag{4}$$

where *he* is the pressure head [m], g was the force due to gravity [m/s2]. Pressure head losses [m] are:

 $he_{loss} = he. he_{nu},$ 

where  $he_{loss}$  is the head losses [m],  $he_{nu}$  is the number of velocity heads. Head losses, presented in pressure units [kPa]:

$$P_{loss} = h e_{loss} \rho g. \tag{6}$$

Then the friction losses in a section of a DH network [kPa]:

$$P_{ft,loss} = 8j \left(\frac{L}{D_i}\right) \frac{\rho v^2}{2},\tag{7}$$

where *j* is the friction factor, *L* is the pipe length [m].

The research is primarily conducted as a case study set in Omsk, Russia. The system is connected to about 12,500 consumers. There are about 14,000 buildings linked to DH system in Omsk, and of these about 70% are residential multi-story buildings. The rest are connections to commercial consumers, and of those the 10 largest customers are connected to the system used in this paper [35]. Most of the consumers are assumed to be equipped now only with two-way valves on the primary side, and this typically applies to the secondary side as well. Three-way valves are assumed to be installed for consumers connected in a way that the return flow is warmer than supply one as in summer mode. The night setback strategy is assumed to happen in 50% of cases in order to reduce the energy consumption during night and use the house's thermal inertia to ensure indoor comfort and save some money.

(5)
The scheme shows five central plants that are represented by CHP ones (steam and gas turbines with gas- and coal-fired boilers), heat-only boiler ones (gas-fired boilers), and the main transmission network, where each line represents both the supply and return pipelines (Fig. 2), whose design temperatures are 150°C and 70°C, respectively.



Fig. 2. Map of the DH network of Omsk

In order to increase the validity of the research supply temperatures and flow rates are actual rather than obtained by simulation. As there are always small measurement errors for all kinds of onsite meters, a note should be given to estimate the influences. The pressure measurement error does not depend on the heat consumption estimation directly, so only the measurement error of flow meter is assumed to be  $\pm 5\%$  and the absolute error of measurement on temperature is  $\pm 1^{\circ}$ C which are common resolutions for a measurement. Measured results are stored like a data set. To create it the Supervisory Control And Data Acquisition (SCADA) was employed. This choice is justified by its common use in the industry. In this case, the PLC S7-200 automation system of the Siemens Co. played a vital role in the quality of the collected data. The Pt100 thermal resistors, the electromagnetic flowmeters and the diffused-silicon sensors are applied for temperature, flow and pressure measurement, respectively.

The total raw dataset spans a period of 24 months, from January 2019 up to December 2020. The reason to choose this particular period is that Omsk has a severe climate with cool winters and hot summers. The average temperature of a cold period is about -14°C. There are historical data on extremes for winter and summer periods in all the regions, but during the winter, strong winds can quickly change the outside temperatures. Therefore, these fluctuations are interesting to track. The theoretical heating period is from September to the following May. During the non-heating period, the DH supplies water for DHW preparation only. The same with Europe, in Russia, engineers designing heating and cooling systems are legally obliged to take them into account when choosing particular technical solution, bud considering extreme and longer observation period adds not only extra value, but also makes the data set more complicated and time-consuming.

### RESULTS



Fig. 3 shows outdoor temperature in Omsk, categorized per two last full years.

Fig. 3. Annual ambient temperature (variation of average daily values)

For the city of Omsk, the ambient temperature is 10°C or less for approximately 3 months of the non-heating period, and less than 20°C for slightly more than 4 months. According to the dynamic reliability, the availability indicators of the network are higher under the same outdoor temperature that takes into consideration the operation and service work [36]. Based on [24], the vulnerable period is when the outdoor temperature is below -14°C. The evaluation of operational state transitions taking into account the variability of the outdoor air temperature is given in [16]. As shown in Fig. 4, the ratio between the conventional regime and the scheduled here, vary widely, but a trend is clear; the DH system may have lower supply temperatures.



Fig. 4. Relation between current normalized system's 2020 temperature profile plotted against the new summer supply temperatures

As can be seen, in the current mode supply temperature in summer is set to 75°C. It accounts 70°C until a heating season ends and has some visible peaks on times when some essential service works are maintained. Whereas the absolute losses become constant (because of the assumed fixed temperature level in the network), heat demand decreases, resulting in higher relative heat losses. This result is well in line with the results found from the survey [20].

To maximize benefit of a novel concept, two-mode system is investigated. In the first case, supply temperature decreases up to 50°C to ensure the DHW demand can be provided. This value was set empirically, since it is the lowest possible value to ensure DHW complying safety regulations. In Ref. [14] the supply temperatures were constrained between a lower limit of 50°C, in order to the DH system will be able to cover instantaneous DHW needs if desired in future upgrades and meet current legislation on legionella control at a substation, and an upper limit of 82°C as used in current British high temperature regulations. Temperature of 50°C corresponds to the conventional level for the whole system: for the sake of simplicity, it is assumed not to vary as a function of instant conditions; so the results are valid for any year [37]. In Gothenburg, Sweden, SH systems operate with supply temperatures of 55°C or less beginning with an outdoor temperature of 5°C [38], i. e. even in winter. Previous works, e. g. [3,39] demonstrated that profiles of a network performance are helpful for optimization methods and the integration of physically constraints based on operational limitations is acceptable. Solutions of the advection-diffusion-heat loss formulas are also analysed under these conditions [12]. As usual [32], limitation is the use of actual case study data, which, in a way, may differ from the exponential correlation to describe the temperature curve used in this paper. It is important to note that this research neither consider the risk of not meeting full demand linked to the use of private units nor the corresponding higher capital costs if entire load is satisfied. The fact that the network cannot adequately satisfy the requested service, even in presence of large capacity, supports the need for an energy accumulator [4]. The most realistic prosumer case for Omsk is probably the 'prosumers intern' case, since the residential areas in Russia are of the second generation and currently not adapted to the lower network supply temperatures. Geysen et al. [13] declare the possibility of manipulating the heat load of a building for a short period of time, typically minutes up to a couple of hours, by adapting the outdoor temperature measurement.

In Fig. 4, the profile is also represented for the second case as temperature for a DH network of 60°C. As known [6], in order to stabilize regime at a heating substation, controller should be tuned considering all the possible operating conditions, i. e. 50 and 60°C modes.

Based on the temperature needs of the DHW systems only, the results of this survey present that the supply temperature in the network may be lowered to 50°C, consistent with 4GDH concept, for more than half of the summer. Depending on the layout, the resulting savings are between 16% and 24%. Optimization in Ref. [17] allows a decrease of about 5.5% in the boiler use and primary energy reduction of 0.8%. The impact of energy-saving, exergy-saving and CO2 emission reduction caused by energy conservation and demand-side structure improvement is up to 20.3% according to [40]. Many utility systems are not constructed specifically for efficiency, but because of urban resiliency or other benefits [23]. Efficiency increases when the temperature level decreases due to the losses of the DH network also decrease. The better working mode is accessed, which gives a better performance.

## CONCLUSIONS

Distributed generation includes different elements of sustainability and supports the authorities in operation strategy. Sizing of the cooling load installation are similarly to common practice (~60% of maximum load) as results emphasize. However, in future value for the 4GDH networks would probably be lower, but in most cases, these networks are site-specific, and the load required for these systems is currently not available in case of Russia within the bibliography. Case study analysed is for city of Omsk, Russia. Assuming DHW load, the summer level is only about 80% of the current temperature. This means that the lowest temperature of 50°C may be achieved through temporary manipulation.

The results obtained indicated that the cooling demand is not met (52% of the reference value) after any year of implementation, due to the fact that outdoor temperature is expected to increase. From the aspect of traditional DH networks, capacity of additional cooling installations is much lower than the required value under the design conditions. Summer operational regime is eligible for current climate conditions, which improve feasibility of the entire system. In addition, the impact of some crucial parameters, such as the network supply temperature and outdoor one, on the energy performance of the distributed cool generation are studied. The resulting savings are between 16% and 24%.

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# REVIEW OF SYNTHETIC INERTIA APPLYING IN THE ELECTRIC POWER SYSTEMS

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### ABSTRACT

Over the world, there is an increasing inclination of installing renewable energy generation sources into electric power systems. The main goal is to replace fossil fuel and nuclear power based generation plants. The continuously shift from classical rotating mass generation to the power electronic based on generation results in a decrease of system inertia. The accompanying loss of rotational inertia and the robust synchronization mechanism provided by synchronous machines and their controls is a challenge to the operation and stability of the electric power systems. As a consequence, during short-circuit in the power system follows the disconnection of the loads or even system split scenarios with significant imbalance, high RoCoF will occur. This article provides a comprehensive review, a classification, and a crucial comparison of different implementation logics and algorithms of the synthetic inertia, highlighting its benefits and drawbacks. Furthermore, the influence of traditional inertia and load regulation for power system stability will be discussed on the article.

**Keywords:** RoCoF, power system inertia, synthetic inertia, rotating mass, electric power system, stability, renewable energy sources

## **INTRODUCTION**

National environmental policies implemented in many countries aim to integrate a large percentage of asynchronous generation into the grid to reduce pollution and produce clean electricity [1]. As a result, increasing number of renewable energy sources are being connected to the grid, most of which are of low/medium power.

The introduction of renewable energy sources into the electricity system raised an important question: what is the impact of these energy generation sources on the stability of the electricity system [2]? Over the past decade, many studies and proposals have been addressed to transmission network operators [3], manufacturers [4], research centres [5] and public associations around the world.

As system inertia decreases, stable system performance may be impaired [6]. This can be especially important in a scenario where more and more renewable energy sources are deployed on the grid and at the same time the system load is low. In such cases, the frequency drop may reach values that will require additional safeguards, such as load shedding [7].

Frequency stability of the system must be ensured in order to maintain load and generation balance. Frequency control can be divided into several stages:

• The initial phase, called inertial frequency response, in which the power of the rotating masses counteracts the frequency deviations from the nominal value [8];

• The second stage, primary frequency control when automatic regulator systems are activated to keep the frequency within acceptable limits;

• The third stage, operation of the secondary regulator by resetting the frequency to its nominal value or close to its nominal value.

Non-inertial generation sources cannot participate in frequency control unless additional control logic is implemented, such as synthetic inertia [9], hidden inertia [10] or virtual inertia [11]. Such additional control logics allow non-inertial generation sources to participate in inertial frequency management by transferring power to the grid from wind parks.

#### FREQUENCE RESPONSE AND SYSTEM INTERIA

Large rotating masses, such as synchronous generators synchronously connected to the grid, have kinetic energy, which is expressed at nominal frequency  $(f_{nom})$  and can be calculated (1) [cond. 12]. Their inertia time constant is calculated by dividing the cumulative kinetic energy in megawatts at synchronous speed by the total power of the electric machine  $(S_{gen})$ . It quantifies the kinetic energy of the rotor at a synchronous speed, expressed in seconds, by how much equivalent amount of electricity the generator should provide when its power is equal to its nominal MVA and is defined (2).

$$E_{kin} = \frac{1}{2} \cdot J \cdot (2\pi f_{nom})^2, \qquad (1)$$

$$H_{gen} = \frac{E_{kin}}{S_{gen}},\tag{2}$$

where: J – moment of inertia,  $f_{nom}$  – nominal frequency,  $H_{gen}$  – inertia time constant,  $S_{gen}$  – rated generator power.

The abovementioned equations show the maximum rated active power duration (in seconds) that a synchronous machine supplies to the grid without any additional mechanical power until it stops. A typical power system consists of a large number of rotating synchronous machines. The total inertia of such a system is calculated by the following formula (3):

$$H_{sist} = \sum_{i} \frac{H_{gen,i} \cdot S_{gen,i}}{S_{sist}} \,. \tag{3}$$

Total system inertia (hereinafter referred to as TSI) is a metric which compute and quantifies the fundamental frequency robustness of an interconnected power system [12]. A direct metric that reflects the levels of TSI is the RoCoF (hereinafter referred to as Rate of change of Frequency) (in Hz/s) in the frequency containment period. Fig. 1. provides a qualitative overview of a typical frequency response following generation outage, indicating the effect of TSI on the initial RoCoF. The response of the whole system depends on the slower responses of Frequency Sensitive Mode control (governor time constants), the faster responses of generation in limited over- and under-frequency sensitive mode control (LFSM-O and LFSM-U) if certain frequency limits are violated, the load sensitivity to the frequency and the frequency containment reserves.



Fig. 1. Effect of TSI on the frequency response

However, most renewable energy sources, such as photovoltaic solar power plants and wind turbines, are connected to the grid via power converters and can therefore be considered system-isolated from the grid frequency.

With renewable energy production and green electricity efforts increasing, energy system operators face major challenges in maintaining the reliability and safety of the electricity system. This increase in sources of non-inertial power in small isolated power systems results in dangerously low levels of inertia and increasing probability of RoCoF detection. Network Codes issued by ENTOS-E attempt to provide additional safeguards and requirements for Transmission Network Operators to ensure power system security and reliability. There are various methods and solutions to ensure total system inertia in order to avoid high frequency crosses and high RoCoF in the electrical system. One way to solve the amount of diminishing inertia in an electrical system is synthetic inertia. Synthetic inertia traditional algorithms and newer solutions are discussed in the next section.

## VIRTUAL INERTIA IN VSM CONCEPT

Virtual Synchronous Machine (hereinafter referred to as VSM) is a generalization of the concept of virtual inertia. VSM is a power source connected to the grid via a converter and capable of responding to abnormal grid fluctuations much like a synchronous generator. This is accomplished by using a synchronous generator model to reproduce its response to voltage, current and frequency fluctuations at the point of connection to the network.

Virtual inertia algorithms are based on the traditional swing equation, restoring the inertia and damping of frequency fluctuations of a traditional synchronous machine [13], [14]. The swing equation used for the implementation is linearized with respect to the speed so that the acceleration of the inertia is determined by the power balance according to (4) [15]:

$$\frac{d\omega_{VSM}}{dt} = \frac{p^{r^*}}{T_a} - \frac{p}{T_a} - \frac{p_d}{T_a}, \qquad (4)$$

where:  $p^{r^*}$  – virtual input mechanical power, p – measured electrical power flowing from the VSM to the grid, and p<sub>d</sub> – damping power, when T<sub>a</sub> is the mechanical time constant.  $\omega_{VSM}$  – the mechanical speed of the virtual inertia in relative quantities is calculated from the power balance integral, and the corresponding phase angle  $\theta_{VSM}$  is calculated from the speed integral. The article [15] provides a block diagram of synthetic inertia of VSM based on the swing equation (Fig. 2)



Fig. 2. Virtual inertia block diagram for estimating frequency droop

From the block diagram (Fig.2.), we can see that  $p_d$  – power damping, which responds to the synchronous machine's power damping effect, is expressed through the damping constant  $k_d$  and the difference between the VSM speed and the frequency of the VSM connected system. On the left side of the block diagram (Fig.2) is a block chart of frequency droop, which is executed by using a cross constant  $k_{\omega}$ , the operating principle of which is based on the difference between the frequency reference  $\omega^*_{VSM}$  and the actual VSM speed  $\omega_{VSM}$ .

The model used in the article [16] is provided in Fig. 3. where the author evaluates primary and secondary frequency control. Inertia constant H and damping factor D evaluate rotor and shaft dynamics. The static coefficient R determines the effect of the primary frequency and  $K_i$  determines the effect of the secondary frequency.  $\tau_1$  is the turbine time constant. The inverter dynamics are defined by the time constant  $\tau_2$ .  $\Delta P_d$  is the difference in active power occurring in the electrical system after abnormal network operation and is expressed in antique units.

Dynamics of rotating mass



Fig. 3. Block diagram of VSM frequency management system

The virtual inertia concept of VSM presented in the article [17] is based on the traditional swing equation (5). The main difference from the already discussed virtual inertia realization principles is that the inertia and damping of a conventional generator is calculated by measuring the power difference between the virtual mechanical power  $P_m$  and the measured electrical power from VSM  $P_{VSI}$ . Damping, which is defined by the damping factor D – the difference between the rotor angular speed  $\omega$  and the nominal value  $\omega_n$ .



Fig. 4. Block diagram of virtual inertia

$$\begin{cases} T_m - T_e - D\Delta\omega = \frac{P_m}{\omega} - \frac{P_e}{\omega} - D\Delta\omega = J \frac{d\omega}{dt} \\ \omega = \frac{d\Theta}{dt}, \ \Delta\omega = \omega - \omega_B \\ E_0 = U_S + I(r_a + jx_s) \end{cases}$$
(5)

where  $T_m~-$  mechanical torque of the synchronous generator rotor shaft,  $T_e-$  stator electromagnetic torque, D is the damping coefficient,  $\omega-$  actual electrical angular velocity,  $\omega_B$  is rated electrical angular velocity,  $P_m-$  mechanical power,  $P_e-$  electromagnetic power, J-rotational inertia,  $\theta$ - electrical angle, E0 is the three phase stator winding electromotive force;  $U_S$ - stator voltage, I- stator current,  $r_a-$  armature resistance,  $x_s-$  synchronous reactance;  $\omega_{VSI}-$  angular frequency difference between VSM rotor angular frequency and nominal value  $\omega_n$ .

Very similar realization of virtual inertia is given in the article [18]. The expression of virtual inertia uses the swing equation which is described:

$$J\frac{d(\omega-\omega_N)}{dt} = \frac{P_N}{\omega} - \frac{P_e}{\omega} - D(\omega-\omega_g) + \frac{1}{\omega D_P}(\omega_N-\omega), \qquad (6)$$

where:  $\omega$  is the rotor angular frequency;  $\omega_N$  is the rated angular frequency;  $w_g$  – network angular frequency,  $P_e$  – electromagnetic active power,  $D_p$  – damping factor, J – virtual rotor inertia.



Fig. 5. Block diagram of virtual inertia with PLL

Fig. 5 presents a block diagram of virtual inertia, which differs from the previous one by using a phase locked loop (PLL) which measures the angular frequency at the point of connection of the  $\omega_{PCC}$  to the network. Such performance of the virtual inertia algorithm when used with PLL affects the accuracy of the calculation of the active power benchmark. It is also difficult to detect transient frequency fluctuations, so PLL is often not used.

## SYNTHETIC INERTIA ALGORITHMS IN A TRANSMISSION NETWORK

Synthetic inertia in the power system shows the power change of the generators in proportion to the frequency derivative of time [19], or RoCoF, since the purpose is to simulate the relationship between the rate of change of frequency and power change characteristic of synchronous machines [8]:

$$\frac{T_{a,G}P_{n,G}}{f_n}\frac{df}{dt} = P_{m,G} - P_{e,G},$$
(7)

where:  $P_{m,G}$ , is the machine mechanical power,  $P_{e,G}$  – the electric power absorbed by the machine load,  $P_{n,G}$  – nominal active pofer of the machine,  $T_{a,G}$  – starting time, f – machine frequency,  $f_n$  – nominal frequency of power system.



Fig. 6. Model of synthetic inertia

Where:  $k_4$  – synthetic inertia controller gain,  $k_1/s$  – single-bus power system model.

The derivative control is effective in reversing the inertia of the power system. Moving the constant  $k_4$  to the right of the power summing unit (Fig. 6) shows how synthetic inertia affects the inertia of a single bus system [20].

#### LINEAR SI CONTROLLER

The author analyses a linear SI controller in the article [21] (Fig. 7). Assuming that the output of the active power  $P_{SI}$  to the controller is relatively fast at the output of the controller, the delay is ignored. In this block diagram upper part is using PD controller, where  $K_{d,SI}$  is the derivative corresponding to the inertia, and the proportional gradient  $K_{p,SI}$  represents the damping. The advantage of this controller is that it simulates the system inertia  $K_{d,SI}$  and damping  $K_{p,SI}$  together. Input also simulates PD – controller with second order filter and power feedback with PI controller, which allows to restore source power.



Fig. 7. Synthetic inertia implementation based on linear SI controller

## CONCLUSIONS

Synthetic Inertia is the ability of a grid-connected power converter to exchange energy when a frequency event occurs. There is not a standard synthetic inertia implementation, although the responses typically involve measuring the frequency and commanding the converter to temporarily increase its active power output. In the literature, several implementations of a synthetic inertia controller have been reviewed, spanning from controls attempting to emulate a swing equation based response from a frequency measurement and a derivative control, droop controllers.

A comparable response to a synchronous machine may be complicated to deliver due to RoCoF measurement delays and filtering. As of today, the response is then better thought of as short term (seconds) frequency response that is delivered through control of the net side inverter.

The reduction in total system inertia significantly affects the capability to provide instantly matching balancing power e.g. for loss of a large infeed.

The main benefit of inertia from synchronous machines is that their rotating mass provides inherently stored energy that, in combination with the voltage source characteristic of a synchronous machine, counteracts voltage angle, amplitude and frequency perturbations and therefore reduces the RoCoF in case of load steps and helps to limit voltage steps by providing a source of active power if needed.

Power system inertia decreasing progressively due to increase renewable energy sources, therefore it is necessary to increase researches in the field of methodologies and algorithm of synthetic inertia to be ready for controlling and maintaining stable frequency in the power system with low inertia.

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# RESIDENTIAL SECTOR ENERGY-SAVING MEASURE ADOPTION STUDY BASED ON BAYESIAN BELIEF NETWORK

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#### ABSTRACT

The European Union set a long-term goal of reducing greenhouse gas emissions by 80-95% below the level of 1990 by 2050. Energy-efficient measures in the residential sector could serve this purpose to a large extent as the housing sector is one of the major sources of energy consumption and carbon emission in the EU. Energy-saving measures in the residential sector could achieve not only energy consumption reduction but also improve living comfort. However, energy-saving measures are not adopted widely, even though many of the measures are proven to be economically viable. This situation creates uncertainty about achieving the greenhouse gas emission reduction goal. How to effectively promote energy-saving is a problem remaining to be solved. A better understanding of the adoption influences is vital for understanding energy saving investment behaviour. This study aims to study the influences of households' decision-making in energy-saving measures in the Netherlands. Both economic and non-economic influences will be studied. Besides, major motivators and barriers will be identified. The study process can be described as follows. First, relevant data is acquired from the WoON (WoonOnderzoek Nederland: Residential Research Netherlands) database. Then, the data will be analysed using the Bayesian Belief Network (BBN) in the software program GeNIe. The characteristics of residential house owners belonging to the categories of energy efficiency adopters and non-adopters will be identified and presented. The analysis results can be used for gaining insights on how to increase energy efficiency measure adoption effectively.

Keywords: Energy efficiency measures; Housing; Decision influences; Bayesian Belief Network

### **INTRODUCTION**

The building sector is one of the main sectors of energy consumption. It accounts for 33% of the total energy consumption in the Netherland in 2018, and residential buildings occupied 61% of energy consumption in the building sector [1]. According to EU directives, the Netherlands set some objectives, such as building-related energy consumption must be less than 507 PJ in 2020 [2]. In 2013, 47 parties, including the government, employers, trade unions, and environmental organizations, developed the Energy Agreement, which includes agreed energy saving targets. The building sector's targets contain an average of 1.5 percent of annual energy consumption saving and 14 percent and 16 percent of renewable energy share in 2020 and 2023 [2].

The energy consumption of the building sector and residential building from 2013 to 2019 is shown in Figure 1. First, there is a considerable gap between the energy consumption in 2019 in the building sector (647 PJ) and the target for 2020 (507 PJ). In general, the energy consumption for both the building sector and residential buildings has a decreasing tendency. However, the average annual reduction rates are 0.88% (residential building) and 1.19% (building sector), both of which did not meet the 1.5% energy consumption reduction target. Renovation for the existing buildings is one of the main obligations from the European Performance Building Directive and a major method for achieving energy saving. The low adoption rate and slow diffusion of energy-efficient renovation are among the reasons for the failure to meet energy-saving targets. Especially for the owner-occupied sector, its renovation rate for all 1-step, 2-step, 3-step, 4-step, and 5-step energy label renovation is the lowest among the owner-occupied sector, social housing, and private rental sector [3].



Fig. 1. Energy consumption for residential building and building sector

Homeowners' decisions are influences by their economic situations [4,5], their attitudes [6], and housing situations [7,8]. This study aims at studying homeowners' decision of housing energy-efficient measure adoptions in the Netherlands and investigating the significant influences of the adoption. Then, policy suggestions are presented based the study results. The paper is structured as follows. Section two introduces the methodology and used data. The third section presents basic description of respondents and reasons for the decision of adopters and non-adoptors. The fourth section describes the study results and discussions. Conclusion and policy recommendations are shown in the last section.

## METHODOLOGY

This section includes two subsections. Subsection 2.1 introduces used data and data sources, while subsection 2.2 demonstrates the analysis method.

## DATA

There are two data sources, the WoON database and the WoON Energy module. The WoonOnderzoek Nederland (WoON) is a large-scale housing market survey conducted every three years. Its topics include housing costs, housing situation and maintenance, and moving behaviour. The database used for this study is version 2018. The WoON energy module is a follow-up of WoON 2018. It includes participants of WoON 2018 who indicated that they are willing to participate in a follow-up investigation. The themes of the energy module are energy labels, housing energy-saving situations, energy-saving behaviours, and adoptions of energy efficiency measures.

Both of the databases contain huge amounts of information, and not all of the information is useful for this research. The used data includes households' socio-demographics, dwelling characteristics, energy-saving behaviour habits, dwelling maintenance adoption, and energyefficiency attitudes.

## **ANALYSIS METHOD**

The analysis method used in this study is the Bayesian Belief Network (BBN). BBN presents the probability distributions over variables. It consists of nodes and arrows and is a kind of directed acyclic graph. Each node represents a variable, and it is associated with a probability table [9]. The BBN can be used for three types of inference. The first type is predictive to investigate the consequences of causes. On the contrary, the second type is diagnostic from the consequences to the likely causes. The omnidirectional mixed inference is the last kind [10]. The second type of inference is used in this study as the aim is to investigate the major influences of homeowners' energy-saving measures.

The basis of BBN is Bayes' theorem, which describes the posterior and prior probability (Eq. (1)):

$$P(A|B) = \frac{P(B|A)P(A)}{P(B)},$$
(1)

P(A) and P(A|B) are the prior and posterior probabilities. P(B|A) is the probability of B given the results of A. BBN could be used to estimate the differences among individuals' value judgement of environment [10], study consumers' behaviour [11], and predict ecological quality [12].

There are various algorithms for learning the structure and parameters of BBN from data. GeNIe provide seven types of learning algorithms, including Bayesian Search, PC, Essential Graph Search, Greedy Thick Thinning, Tree Augmented Naive Bayes, Augmented Naive Bayes, and Naive Bayes. This study adopted PC algorithm as it is one of the earliest and most popular algorithms. This algorithm uses the observed independences in data to generate networks' structures.

The study process includes three steps. The first step is going through the two databases and selecting out the needed data and form new data files. The second step is processing the data. As described in section 2, only respondents indicated participating the follow-up survey joined the energy module. There are much less participant in the energy module compared with the WoON 2018. During this process, we merged the two data file through the respondents' ID; energy module respondents 'information from WoON 2018 was imported. Non house owner respondents and respondents with missing data were filter out when processing the data. After the case filter process, there 2456 cases left. The last step is analysing the data. First, a descriptive analysis is presented, then GeNIe is used for further analysis. The target variable for the analysis is the adoption of energy-saving measure. In the Energy module, respondents were asked whether they adopted any Energy-Saving Measures (ESM) in the past five years,

which is the basis of the target variable. The variables need to be distributed into different levels for analysing. The variables and its level are presented in Table 1.

Variables	Levels	Note	Variables	Levels	Note
Socio demographics			House characteristic		
	17-34	0	& maintenance		
age	35-74	1		<40	0
-	75 and older	2	a_surfacearea (house	>=40 & <60	1
	Low and	0	surface area per person)	>=60 & <90	2
ad (advantian)	unknown			>=90	3
ed (education)	High school	1		Flat and others	0
	high	2		Terraced	1
a income (household	<15	0	hou_typ (house type)	house, corner	
a_income (nousenoid	>=15 & <35	1		Semi-detached	2
moome per person per	>=35 & <55	2		Detached	3
year, '1000 euros)	>=55	3		A &A+	0
hou com (household	Single person	0	ener label (energy	В	1
	& 1 parent&		label)	С	2
	non family			D, E, F &G	3
composition)	Couple	1		<50	0
	Couple	2	a_enerbill (energy bill	>=50 & <80	1
	+child(ren)		per person)	>=80 & <120	2
Environmental				>=120	3
attitude			in main (indoor	No	0
atti_hou (house must	Agree	0	maintanence adoption)	Yes	1
become more energy	Neutral	1	out_main (outdoor	No	0
efficient)	Disagree	2	maintenance adoption)	Yes	1
atti_ee (Energy-	Totally agree	0	Energy efficient		
efficient homes	Agree	1	beahviours		
contribute to a liveable	Neutral and	2	EEB g (adoption	<=2	0
planet)	disagree		number of energy-	3&4	1
per_ec (your household	More	0	efficient behavior)	More than 4	2
uses more or less	The same	1	EEB attitude	very important	0
energy than other	1000	2	(importantce of energy-	important	1
households?)	1033		efficient behaviour)	others	2

Table 1. variables and levels

# **DESCRIPTIVE ANALYSIS**

## **Basic information**

The respondents' age distributions and their dwellings' construction years are shown in Table. 2 and Table. 3, respectively.

Age group	17-24	25-34	35-44	45-54	55-64	65-74	75 and older
counts	15	209	312	371	634	685	230
Percentage (%)	0.61	8.51	12.70	15.11	25.81	27.89	9.36

Table 2. Respondents' age distribution

Construction year group	Before 1930	1930- 1960	1960- 1970	1970- 1980	1980- 1990	1990- 2000	After 2000
counts	338	346	251	476	365	364	316
Percentage(%)	13.76	14.09	10.22	19.38	14.86	14.82	12.87

Table 3. Housing construction year distribution

The two tables give general information about the situations of the respondents and their living situation. As shown in the figures, most of the respondents are older than 54. More than half of respondents fall into the age group "55-65" and "65-74". Most housings are built after 1970, and the group with the highest percentage is the group of "1970-1980", about one-fifth.

## Reasons for adopters and non-adopters

In this subsection, reasons for adoptors and non-adopters will be presented. The provided energy-saving measure options in the survey include: 1) double glazing fitted, 2) additional windows placed, 3) insulation of roof, wall, floor or walls installed, 4) solar panels installed or replaced, 5) installed or replaced the central heating boiler or other installations, 6) other energy-saving measure (s) carried out, and 7) no energy-saving measures implemented.





Fig. 2. Reasons for adopting energy-saving measures

Fig. 3. Reasons for not adopting energy-saving measures

Results show that 794 respondents (32.33%) do not adopt any energy-saving measures, and 67.67% of them (1662 respondents) carried out energy-saving measures. Reasons for

implemented energy-saving measures and did not implement energy-saving measures were also asked in the survey. The top seven reasons for adopters and non-adopters are shown in Fig. 2 and Fig. 3.

About 27% of the ESM adopters referred "lower utility bill" as one of the main reasons. Another economic reason is increasing home value, recognized by 118 respondents. Three reasons are housing comfort-related, which are "making the home more enjoyable", "needed maintenance", and "fight ventilation or moist problems". They rank second, third, and sixth, respectively. Considering the environment rank fourth, and it is referred by 279 respondents. These statements of lower energy bills, protecting the environment, needed for maintenance, and increase housing value are in accordance with the finding in most studies [8,13,14].

The first-ranking reason for not adopting ESM is the house is already energy-efficient, which is recognized by nearly half of the non-adopters. No time and not think about it is the second reason. Economic-related reasons include "I cannot afford this" and "not enough savings," ranking third and fifth, respectively. The fourth reason is information related. Finding professionals and getting information are identified transaction costs and barriers of energy-efficient renovations [15]. These reasons were always presented as adoption barriers. The presented statements are common in studies, including economic reasons, information limitation, and attitudinal reasons [14,16–18]. What is more, 29 respondents stated that the reason for not adopting ESM is VvE (Homeowner association) does not want this.

## RESULTS

This section presents the BBN analysis results. Influences' significance is described, and major influences are identified. This study aims to identify the importance of the variable on households' EMS decisions. The BBN result is shown in Fig. 4. The nodes of the BBN are in different shades, which is based on the sensitivity analysis results. The deeper shapes imply a more significant influence on the target variable: ESM adoption. The different coloured rectangles present the four categories of variables, which in line with Table 1. In the following subsections, these variables and their influences will be discussed in detail.



Fig. 4. BBN result

## **Socio-demographics**

Four socio-demographic variable were included in the study: age, education, household average income, and household composition. As presented in Fig. 4, home owners' age and household composition have greater influence on ESM adoption decision compared with education and income. The detailed results of age and household composition are shown in Table 4. The income and the education variable is not presented as there is no numerical difference between different levels. As shown in Table 4, home owners in the 17-34 age group are 4% less often for adopting ESM then the overall adoption rate of 68%, and there are only 9% of the respondent belongs to this age group. Single person, one parent and non-family households are 3% less often for choosing ESM compared with the 68% overall adoption rate, while households of couple and child(ren) are 2% more often. These two factors do not directly influence the ESM adoption decision. They influenced the adoption decision through the house type factor as shown in Fig. 4. In general, 18% of respondents live in apartments. However, 37% of age group "17-24" and 24% of age group "75 and older" live in flats. And 35% of the first-level household composition respondents lives in flats.

Sacia dama manking	Respondents	ESM a	D:fformer and	
Socio-demographics	percentage	Yes	No	Differences
age				
17-34	9%	64%	36%	-4%
35-74	82%	68%	32%	0%
75 and older	9%	67%	33%	-1%
Household composition				
Single person & 1 parent & non family	26%	35%	65%	-3%
Couple	48%	32%	68%	0%
Couple +child(ren)	25%	30%	70%	2%

Table 4. Results of socio-demographic factor

## House characteristic and maintenance

In the house characteristic and maintenance category, three factors significantly impact the adoption decision: house type, indoor maintenance adoption, and outdoor maintenance adoption. And the impact is direct as these factors are directly connected with the target variable. The results of the three factors are shown in Table 5. The first level of house type is flat and others, flats accounted for about 97% while others only occupied about 3%. The "others" building type include farm, the house with garden business, the house with separate shop, office, and practice. Homeowners of flats and other houses are significantly less likely to adopt ESM than the average, with 13%. These results is in consistent with studies such as [7]. Households adopted indoor maintenance are 16% more likely adopted ESM compared household without indoor maintenance. Moreover, households without outdoor maintenance are 10% less often of adopted ESM compared with the overall adoption rate (68%).

Sasia domographics	<b>Respondents'</b>	ESM a	Differences	
Socio-demographics	percentage	Yes	No	Differences
House type				
Flat and others	18%	53%	47%	-13%
Terraced house, corner house	40%	70%	30%	2%
Semi-detached	20%	71%	29%	3%

Table 5. Results of socio-demographic factor

Detached	22%	73%	27%	5%
Indoor maintenance				
No	50%	60%	40%	-8%
Yes	50%	75%	25 %	8%
Outdoor maintenance				
No	26%	58%	42%	-10%
yes	74%	71%	29%	3%

#### Environmental attitude and energy-efficient behaviours

As shown in Fig. 4, the number of household energy-efficient behaviours directly impacts the ESM adoption. The attitude towards energy-efficient behaviours also impacts to some extent, but not as great as energy-efficient behaviour adoption. However, the impacts of environmental attitudes are not obvious. The higher the number of adopted energy-efficient behaviour, the more likely of adopting ESM, and households with more than five types of energy-efficient behaviours are 4% more likely to adopt ESM. Households with negative energy-efficient behaviour attitudes are 4% less often for adopting ESM.

## CONCLUSIONS

This study used the Bayesian belief network to not only identify the significant influences of energy-efficient measures adoption in households, but also how much or less likely that household with certain features will adopt energy-efficient measures. Results in this study in lines with most of the existing studies. There are also some differences, such as that old homeowners (age group of 75 and older) are less likely to adopt energy-efficient measure in this study, while [7] suggest that elderly households are more likely to adopt energy-efficient measures. According to the study results, households' ESM adoption decisions are sensitive to seven of the analysed variables, which are age, household composition, house type, indoor maintenance, outdoor maintenance, energy-efficient behaviour, and energy-efficient behaviour attitude. Even though 27% of the ESM adopters consider "lower energy bill" as the reason of adopting ESM, the difference in ESM adoption among different income levels is not significant. The environmental attitudes also have little impact on ESM adoption decisions. Most of the respondents have positive and responsible environmental attitudes; however, the positive attitudes do not lead to ESM adoptions. This phenomenon is described as "knowledge-action gap" and "value-action gap" [16]. On the contrary, households' energy-efficient behaviour adoption implies that they are willing to take actions to save energy. Age and household composition influence do not influence the ESM adoption directly. However, different age and household composition groups have different housing type preference, which has major impacts on ESM adoption. For example, homeowners under 24 years old and older than 75 years old are more likely to live in apartments, and apartment homeowners are significantly less likely to adopt ESM.

The governments can promote ESM in apartments and terraced house, as they have a lower ESM adoption rate, especially for apartments. Another option is to work with housing renovation contractors to providing more information about ESM. There are several reasons; firstly, homes that had maintenance are more often adopted ESM. Secondly, not knowing the options is the fourth-ranking reason for not adopting ESM.

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# CHARACTERISTICS OF THE COMPRESSOR FOR A HEAT PUMP OF AN AIR HANDLING UNIT

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#### EXTENDED ABSTRACT

#### **OVERVIEW**

Energy consumption in buildings is increasing every year. The main consumers in buildings are heating, ventilation and air conditioning (HVAC) systems, which consume half of the energy consumed by the European Union (EU), of which a lot is lost due to inefficient use [1]. It is HVAC systems that require new solutions that open opportunities for creating more efficient products that directly contribute to the achievement of the strategic goals of the EU and Lithuania to reduce energy consumption, use renewable energy sources and improve energy efficiency. The use of heat pumps for heating systems in buildings is not new, but their use in ventilation systems is less common. Recently, the situation has begun to change, more and more manufacturers of ventilation units (e.g., FläktGroup, Mandik, Dantherm A/S, Komfovent, VENTS) offer air handling units with built-in heat pumps [2]. The energy conversion modes of such devices are permanently changing in accordance with the constant change of the outdoor air state (temperature, humidity). Flexibility, the ability to rationally respond to permanently changing ambient air parameters is an important feature of the choice of operating mode of energy transformers and its control. The overall seasonal efficiency of the air handling unit depends on it. The main component dictating the operating mode of the heat pump is the compressor. The change in its operating characteristics should be defined by the functional purpose of the heat pump. At each outdoor temperature, the compressor must have a specific combination of pressure ratio and flow rate. Theoretical models and experimental studies of heat pump compressors are presented in the scientific literature, in which the issues of compressor operation efficiency are analysed. However, these works are more focused on the operating parameters and efficiency of the compressor, little attention is paid to the thermodynamic cycle of the heat pump and its demand. No attempt is made to follow the specific needs of changing the cycle with a compressor. The issue is viewed from the perspective of design solutions, not from the optimal demand mode. This work is aimed at finding out what should be the characteristic of the compressor that effectively operates in the heat pump of the air handling unit, corresponding to the given operating character of the heat pump. More precisely, its specific evolution of the cycle with changes in the outside air temperature.

#### **METHODS**

The article analyses the processes of energy transformations in the air handling unit (AHU), the main energy transformers of which are heat pump (HP) and heat exchanger (HRE). HP consists of condenser (CN), evaporator (EV), compressor (CM) and throttle valve (TV). Along with two fans (supply – Fs and exhaust – Fe) and the aforementioned ventilation heat recovery exchanger (HRE) we have an AHU. The interaction parameters of these components under typical AHU operating conditions are analyzed in this work. In the context of this study the characteristic operating conditions include states of the ambient and ventilated room air and HP refrigerant states, primarily characterized by temperatures.

Thermodynamic processes (primarily heat transfer, transfer rates) of heat exchangers (HRE, CN, EV) of an air handling unit are considered similar. The combination of energy balance equations for these heat exchangers reflects the thermodynamic operation of the air handling unit.

From a numerical point of view, the properties of the selected refrigerant are important, but it is assumed that their influence on the processes in the air handling unit is not more special than in other cases of the reverse cycle. The refrigerant R410A is used in this study.

9 variants of air handling units with different combinations of specific heat flow rates (Ak) of heat exchangers (CN, EV) were selected for the analysis.

#### RESULTS

The change in the compressor characteristic is determined by the functional purpose of the heat pump; at each outdoor temperature  $(T_e)$  it must have a certain combination of pressure and flow rates of refrigerant.

The results presented in the article show the dependences of the high- and low-pressure ratios of the heat pump operating cycle of all the considered air handling unit variants on the relative flow rate of the refrigerant. These curves reveal the performance characteristics of the heat pump compressor at specific condenser and evaporator specific heat flows.

#### CONCLUSIONS

A parametric analysis has been performed. The algorithm applied to it makes it possible to determine the required change of isotherms of the operating cycle of the heat pump depending on the outside air temperature, the characteristics of the accompanying compressor, the possibility of its combination with heat exchangers of heat pumps.

Keywords: air handling unit with integrated heat pump, compressor characteristics, variable outdoor temperature

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# THE REVIEW OF IMPLEMENTING HOUSEHOLD ENERGY SAVING TARGETS FOR CLIMATE CHANGE MITIGATION

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#### ABSTRACT

The paper discusses measures to reduce energy consumption in households, examines their application, the willingness to pay of the population for energy efficiency and the use of renewable energy increase in households in the light of the research which were done recently. Households account for 72% of total greenhouse gas emissions. Thus, they are key factors in reaching the 1.5 °C goal under the Paris Agreement. Research shows that the use of insulating materials in renovation of building constructions reduces the need for energy and residents are willing to pay extra for it. However, it should be emphasized that the willingness to pay for energy savings is closely linked to the wealth of the owners, and also household owners are placing an extra willingness to pay value on most noticeable (like aesthetics), but non-energy benefits of the investment. Many studies focus on the impacts of various determinants and/or willingness to pay for various types of appliances when energy efficiency labelling is introduced, however, this review shows, that short term voluntary efforts will not be sufficient by themselves to reach the drastic reductions needed to achieve the 1.5 °C goal. Instead, households need a regulatory framework supporting their behavioural changes. Studies have shown that changing household behaviour can lead to significant energy savings, resulting in lower greenhouse gas emissions, helping to meet greenhouse gas reduction targets and improving the well-being of the population.

Understanding and targeting the behaviour of citizens in terms of private household energy consumption and conservation is essential in achieving energy efficiency targets. Financial incentives and education could contribute to changing consumer's behaviour to mitigate climate change. However, there are many behavioural barriers for changing the behaviour of the population. Therefore, this article also addresses behavioural barriers to sustainable energy consumption in households and provides a structured set of measures that could help to overcome these barriers.

Keywords: climate change mitigation, households behaviour, energy saving, behavioural barriers.

#### **INTRODUCTION**

Globally energy savings play an essential role in fulfilling climate change mitigation objectives and consequently understanding the take up of energy efficiency retrofits and their influence on energy demand. Variations in these retrofits across the population is vital to comprehend their potential as outlined in Hamiltos, I.G et al. (2016) [1]. In order to stop global warming to 1.5°C and reach the climate and energy targets set by the Intergovernmental Panel on Climate Change (IPPC) [2], by the European Commission [3], and by the Paris Agreement [4], countries across all sectors encouraged to be motivated to make environmentally sustainable choices. Such motivation measures like monetary savings, smart technologies, feedback systems are already being implemented in several countries [5]. Unfortunately, energy efficiency approaches alone are unlikely to deliver anywhere near the energy reductions needed in the limited time available, however, all energy reductions will have to come from energy conservation, involving less use of energy-using devices, including private vehicles. Achieving such reductions will require changes in lifestyles, especially for residents of non-OECD nations as outlined Moriarty P. and Honnery D. (2019) [6]. Considering this, a wide range of climate change mitigation policies have been developed globally and these policies have become one of the biggest concerns. Though discussions are still needed about effective climate change mitigation policies that might be commonly acknowledged by society in general [7].

A large number of research investigates the links between consumer socio-demographic characteristics, norms and attitudes and energy efficient habitual and/or occasional behavioural choices, among which choices of home appliances. Various hypotheses were put forward, such as that environmental sustainability behaviours is influenced by demographic factors, awareness, knowledge, social norms and price of appliances. The possible contribution and position of households in climate policies is neither well understood, nor do households receive sufficiently high priority in current climate policy strategies. Households are generally believed need to change their actions in order to mitigate the challenges posed by increasing fossil oil consumption levels. [8] Therefore, this article also reviews the behavioural barriers that hinder the achievement of energy saving goals in households and the policies designed to overcome these barriers. The following aspects are discussed in more details: 1) Renovation and "Green buildings"; 2) Choosing more economical devices; and 3) Behavioural barriers for energy saving in households.

# RENOVATION AND "GREEN BUILDINGS" IMPACT ON ENERGY SAVINGS IN HOUSEHOLDS

Scientists agree that reducing greenhouse gas (GHG) emissions is one of the key goals in order to contribute to climate change mitigation for households [9, 10]. There are final energy demand scenarios for 2015, 2050 and 2100 provided for reducing CO<sub>2</sub> emissions to achieve the 2050 carbon level target [9, 11]. Levesque A. et all [11] presented the scenario results for final energy demand at the global level. There the authors claim, that in 2050, the Reference scenario shows a strong increase in the aggregate demand (+62%) spurred by a growth in appliances and lighting consumption, space cooling and water heating. In 2100, this pattern is accentuated with a doubling of the demand compared to 2015 (+126%). However, the findings show that energy-saving renovations can substantially reduce energy consumption and CO<sub>2</sub> emissions in existing buildings. [13]

Research [11] shows that renovation of buildings, where the usage of insulating materials in construction reduces the need for energy and residents are willing to pay extra for it. However, it should be emphasized that the willingness to pay (WTP) for energy savings is closely linked to the wealth of the owners, and also household owners are placing an extra willing to pay value on most noticeable (like aesthetics), but non-energy benefits of the investment. It demonstrates, that householders who stated lower familiarity with the Green buildings concept, were WTP a lower price premium then those with higher familiarity. In Table 1 are provided review measures to promote the renovation of residential buildings.

Measure to promote	The main findings of researches	References
the renovation of		
residential buildings		O 11' M 1
Information/	• Higher costs reduce the probability of a retrofit	Collins M. and
advantages of	option to be chosen, but in contrast to nouseholds	Curus J. (2018)
renovation	conceivable to choose a pricier repovation than	Bhochhibhova
	homes upgrading by energy efficiency retrofit	S and al $(2017)$
	means for the first time:	[15]
	• Emission of pollutants from fuel wood and cattle	
	dungs used for space heating can be reduced by	
	increasing efficiency of the building.	
	• Locally available materials cum waste products can	
	be used as building insulation cost effectively.	
Government initiatives	• Grants and subsidies; Tax incentives; Loans	Leung B.C.M.
	Researches notes that without local government	(2018) [14]
	funding and motivation for greening the existing	Bertoldi P. et al,
	buildings (GEB) strategy, long-term ecological	(2020) [16]
	understanding and implementation can be	
	unsustainable.	
Fnergy demand	• Demand side management and renewable energy	Levesque A
regulation	have a great potential in to mitigate the climate	and al
	change impact as a local effort:	(2019) [11]
	• To maximize the co-benefits achieved with energy	Bhochhibhoya
	related renovation measures, all main elements of	S.
	the building envelope should be improved to a	and al
	minimum energy performance dimensioned	(2017) [15]
	according to the local climate;	Ferreira et all
	• Halving energy demand from buildings: The	(2017)[17]
	adoption of low consumption practices can save as	
	much as 61% of the energy that would be consumed	
Consumer behaviour	by 2100 in the reference scenario	Colling M and
changing and	• Customers are winning to pay a premium for reatures	Curtis I $(2018)$
Willingness to pay for	• Stated willingness to pay is roughly additional 5%	[13]
green apartments	for low-energy buildings is a rational investment	Zaleiska-
8 · · · · · · ·	decision:	Jonsson A.
	• Use of three categories to explain the level of free-	(2014) [18]
	riding application which may or may not possess:	Streimikiene D.
	i.e. 'Free-riders', 'Partial free-riders' and	and al
	'Dependents';	(2011) [19]
	• The negative effect of cost on renovation option is	
	much stronger in less energy efficient homes, in	
	comparison to more energy efficient homes;	
	• Measures to change household behaviour can	
	generate significant energy savings, leading to	
	I lower greenhouse gas emissions, lowering national	

Table 1. Promotion of the renovation of residential buildings

greenhouse gas reduction targets and improving the well-being of the country's population	
wen-being of the country's population.	

Home retrofits help to ensure the long-term stability of residential facilities by conserving capital and energy and increasing the quality of internal operations. [20] Energy consumption from activities in buildings at the end of the century would decrease by 11% compared to the 2015 level, instead of a 126% increase. The decrease in energy demand is driven by new practices for hot water usage, insulation and by the increased use of efficient air conditioners and heat pumps [11]. Dubois et al. [21] performed the research and stated, that household living situations (demographics, size of home) greatly influence the household potential to reduce their footprint, even more than country or city location. Having children and buying a new home are significant factors pushing the  $CO_2$  emission curve upwards. So, if people during this period were encouraged and realised the benefits of the "Green Building" purchased, these emissions could be reduced. Therefore, government programs and education would be much needed during this period. In addition, Dietz Th. With colleagues (see Ref. [22] for more details) have found that the national reasonably achievable emissions reduction can be approximately 20% in the household sector within 10 years if the most effective non-regulatory interventions are used.

# CHOOSING MORE ECONOMICAL DEVICES FOR ENERGY SAVINGS IN HOUSEHOLDS

Increasing the efficiency of all energy-using devices, or reducing their use by any means are the two approaches for reducing energy consumption [6]. Many countries around the world have introduced mandatory energy-efficiency labelling standards for appliances, which provide information on the energy used by appliances to increase their efficiency. Besides, many studies [23, 24] focus on the impacts of various determinants and/or WTP for various types of appliances when energy efficiency labelling is introduced. The information on yearly energy costs strongly increases the chances that consumers choose the more cost efficient appliance. Research results emphasize that informed and rational choices of appliances could be enhanced by the provision of monetary information on yearly energy consumption. First, with an obligation for the producers of electrical appliances to provide information on the future energy consumption of the product in the form of a monetary estimate. A second strategy would be to educate consumers about the energy consumption of different appliances and how to identify the most efficient appliances by means of brochures and energy literacy courses at schools [25].

Policy-making tools such as changing consumers' perceived psychological benefits of using energy-saving products through public advertising can help make consumers "feel good while doing well" socially and environmentally [26].

Table 2 represents in more detailed the reasons of the choice of more economical appliances in households.

Reason of the choice of energy saving device	The main findings of researches	References
For energy savings / lower bills	<ul> <li>The information on yearly energy costs strongly increases the chances that consumers choose the more (cost-)efficient appliance;</li> <li>Informed and rational choices of appliances can be enhanced by the provision of monetary information on yearly energy consumption;</li> </ul>	Blasch J. et all (2019) [25] Darby S. (2006) [27] Ramos A. et al, (2015) [28]

Table 2. Reasons of the choice of more economical appliances in households.

	<ul> <li>Households that purchased energy-efficient air- conditioners saved more electricity than those that did not;</li> <li>Data on the use of electricity by households (feedback) can decrease energy consumption.</li> </ul>	Mizobuchi K. and Takeuchi K. (2016) [29]
Due to pro- environment behavioral	<ul> <li>Environmental attitude and concern, as well as psychological benefits, have a significantly positive impact on respondents' behavioural intention to buy energy-saving devices;</li> <li>Altruistic attitude is associated with more active participation in power saving;</li> <li>The rebound effect can cancel out the energy-saving benefits of powerful appliances. As example, "Additional-purchase households" showed significant energy savings, whereas "replacement households" did not;</li> <li>Age and household size significantly and positively correlate with purchasing energy-saving appliance decision.</li> </ul>	Xianchun L. et al (2020) [26]
Due to governments regulation	• With a stronger government call to save electricity, households are saving more energy.	Mizobuchi K. and Takeuchi K. (2016) [29]

Households can save money and reduce their energy consumption by buying more energy-efficient appliances and implementing energy-saving habits. As traditional appliances play a key role in meeting primary needs, they are mainly found in household dwellings, and their potential contribution to reducing overall energy consumption is still very high. Studies have confirmed the cost-effectiveness of energy efficiency benefits from electrical appliances compared to other sectors. [30] Research by Borg and Kelly (2011) [31] has shown that switching to more efficient appliances can reduce average electricity consumption by 23%. However, various policies are needed to accelerate the trend for more consumers to make the decision to buy energy-efficient appliances instead of standard appliances. One possible measure is a legally enforceable minimum level of energy efficiency, called minimum efficiency standards. Price regulation through the phasing out of fossil fuel subsidies would also lead to more energy efficiency. Another possible tool is to provide information on available technologies, such as an energy labelling scheme, to help consumers understand which products are the most efficient and what are the benefits of this efficiency. [32]

# **BEHAVIOURAL BARRIERS FOR ENERGY SAVING IN HOUSHOLDS**

Energy saving in households depend to a large extent on consumer decision-making. As a result, many scientists [33, 34, 35] take into account the insights of behavioural economics and argue that lifestyle and behaviour change are key tools for achieving household energy reduction goals. Behavioural barriers include spending patterns, a misconception of economic returns, a variety of purchasing options, a lack of confidence in local and national government, low cost-effectiveness of expenditure, a lack of appealing goods and services, and a desire for convenience. The majority of the time, these impediments are triggered by a lack of awareness, which has an effect on both enhancing energy quality and implementing energy-efficient technologies. [36, 37, 38, 39] In Fig. 1, we can see behavioural barriers to reducing energy demand in households and policies to overcome these barriers.

**Behavioural barriers:** 

#### Policies that may help it address

•Uncertainty on renovation costs/benefits and payback

Information

Audits, labelling of products;
Programs that expected consumers to focus on losses rather than benefits. Fig. 1: Behavioural barriers to reducing energy demand in households and policies to overcome them. [40; 41; 42]

Users' assessments of incorrect habits have a negative effect on energy demand. The energy benefits of an energy retrofit design can be influenced by occupant behaviour, which lengthens the investment's payback period. [43] Research show, that public awareness of energy efficiency and environmental concerns could be increased in order to encourage the adoption of energy-saving alternatives. [44] Therefore, researchers [45, 46, 47] suggest using "Boost" (based on enhancing human competencies) and "Nudge" (based on human's deficiencies in the cognition or motivation of individuals 'intuitive system) interventions to achieve energy reduction goals. This interventions can be effective in achieving policy goals and reducing government spending, particularly in areas where traditional policy interventions are difficult to control, such as energy consumption. [48]

## CONCLUSIONS

Based on collected information from the different scientific reviews, the following conclusions could be drawn which are mainly focused on changing consumer's behaviour to improve climate change mitigation. Firstly, the main finding was that energy efficiency approaches alone are unlikely to be sufficient to achieve the reduction in energy demand that needs to be achieved during the limited period of time. Instead, most energy reductions will have to come from energy conservation, involving less use of energy-using devices, including private vehicles. Achieving such reductions will require changes in lifestyles, especially for residents of non-OECD nations.

Secondly, the greatest part of researches shows that renovation of buildings and the use of insulating materials in construction reduces the need for energy, thus residents are willing to pay extra for it. However, it should be emphasized that the willingness to pay for energy savings is strongly linked to the wealth of the owners, and also household owners are placing an extra willingness to pay value on most noticeable (e.g. aesthetics), but non-energy benefits of the investment. In addition, many studies focus on the impacts of various determinants and/or willingness to pay for various types of appliances when energy efficiency labelling is introduced.

Finally, studies have shown that changing household behaviour can lead to significant energy savings, resulting in lower greenhouse gas emissions, helping to meet greenhouse gas reduction targets and improving the well-being of the population. However, there are many behavioural barriers to changing household behaviour. To promote energy savings in households through housing renovation and energy-saving appliances, economic benefits, as well as public education, should be prioritized by policymakers. In order to raise public awareness of energy saving and environmental concerns, it is recommended to promote energy saving opportunities that can help achieve greenhouse gas reduction targets and improve the well-being of the population. It should be emphasized that non-monetary nudge and boost interventions are increasingly recommended for behaviour change.

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# EVALUATION OF ENERGY VALUES DURING THE HEATING OF THE MODEL SUGAR SOLUTION USING A OHMIC SYSTEM

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#### ABSTRACT

The use of current electrical heating applications is increasing depending on the developing technology. One of these methods is ohmic heating. The ohmic heating process is the generation of heat in the product by passing alternating current between two electrodes and as a result, the product is heated. The ohmic heating is known as a homogeneous, efficient and fast heating method. The novelties of this study is the absence of studies in the model solution using the Ohmic heating process and also not specifying the changes in the model solutions in this heating process. In this way, it is aimed to provide data about the changes that occur especially in different sugar concentrations. The main purpose of the present study was (I) heating the pH 3.5 sugar solution, which had 4 different Total Soluble Solid Content (TSSC) (10-40%), from 10 °C to 95 °C, (II) determination of total energy consumed for the ohmic heating and (III) the average power values of the system. The ohmic heating system consisted of a computer, isolated transformer, test cell (Polyoxymethylene), electrodes and a custom made microprocessor. The temperature inside the product was determined with a T-type thermocouple, and the temperature, current and voltage values were recorded every second. It was determined that the total spent energy in the ohmic heating process increased from 45.8 kJ to 53.0 kJ as the TSSC value increased. In addition, the average power value of the ohmic heating system had changed depending on the TSSC value. It was determined that the highest power value was 161 W at 10% TSSC sugar solution, while the lowest average power value was 72.8 W at 40% TSSC. Energy efficiency was reduced as TSSC value increased which is indicated by statistically negative significant difference (p < 0.05). It showed that the TSSC value of the sugar solution had an effect on the total energy value, average power value and energy efficiency during the ohmic heating process.

Keywords: Ohmic heating, Energy, Sugar Solution, Efficiency

#### **INTRODUCTION**

Due to the developing technological processes, the demand for highly efficient and environmentally friendly heating processes in the industry is increasing. The food industry generally prefers indirect heating. Steam is produced especially by using fossil fuels, which means higher costs for the industry. Since the use of fossil fuels harms the environment, researchers are looking for alternative heating techniques. Microwave heating (Sarah, Hanum, Rizky, & Hisham, 2018), ultrasound heating (Bagherian, Zokaee Ashtiani, Fouladitajar, & Mohtashamy, 2011), pulsed electric field heating (Chemat et al., 2017) and ohmic heating (Icier, Yildiz, Sabanci, Cevik, & Cokgezme, 2017a) process draw attention among the current heating techniques that are increasingly used in the industry. It is seen that the use of ohmic heating, which is one of these heating techniques, in industry is increasing.

The Ohmic heating process is based on the heating principle of the product by passing alternating current through the product between the two electrodes, causing the generation of heat in the product. Ohmic heating process is expressed as a homogeneous, fast and efficient heating especially for liquid products. It has been reported that the content of the product used in the Ohmic heating process has an effect on the applied energy and the processing time (İçier, 2012).

The Ohmic heating method is increasingly used in food processing. When current publications are analysed, this method is used in extraction, evaporation, cooking, dissolving and heating applications (Cevik, 2021; Cevik & Icier, 2020; Cokgezme, Sabanci, Cevik, Yildiz, & Icier, 2017; Döner, Çokgezme, Çevik, Engin, & İçier, 2020). In these studies carried out with Ohmic heating application, the heating time of the product, electrical conductivity values and performance were evaluated. In addition, it was determined that the homogeneity of warming in food was examined by thermal imaging processes. In addition, it was determined that some studies focused on the change in the quality characteristics of the product (Sabanci, Cevik, Cokgezme, Yildiz, & Icier, 2018).

It has been determined that the Ohmic heating process is mostly focused on products such as fruit juice, meat, milk and fish (Cevik & Icier, 2018; Icier et al., 2017a; Li & Sun, 2002; Ruan, Ye, Chen, Doona, & Taub, 2002; Suebsiri, Kokilakanistha, Laojaruwat, Tumpanuvatr, & Jittanit, 2019). It has been found that ohmic heating studies, especially using model products, are quite limited. The most important criterion on the heating of product with Ohmic process is the ionic mobility of the product. It is not possible to heat pure water with the ohmic system because there is no molecular or ionic activity in it. It is known that pH value is an important criterion for ionic mobility in fruit juices. Fruit juices have different sugar content and pH values or after the applied processes (e.g.: evaporation) there is serious sugar content increases occur in the solutions, and the effects of these differences on heating have not been fully expressed. For this reason, sugar content is one of the most important factors limiting molecular mobility in ohmic heating process. For this reason, in the present study, it is thought that examining the changes in a model product in order to answer this question (relation between sugar content and heating) in fruit juices will contribute to the literature. Therefore, the main purpose of the present study is to heat the glucose syrups that have different sugar contents after adjusting to the desired pH values with citric acid and to evaluate the performance values (energy and power) at the end of the heating process.

## **MATERIALS AND METHOD**

#### Materials

Model solution was used in the present study. Distilled water and glucose syrup were mixed to prepare the model solution. In addition, citric acid, which is widely available in nature, was used to adjust the pH value. The glucose syrup used in here had a total soluble solids content

(TSSC) of 80% and was diluted with distilled water to the target TSSC content (10%, 20%, 30% and 40%). The pH value of the sugar solution in the target TSSC value was adjusted to 3.5. The prepared model solutions were placed in a refrigerator at 4 °C and stored until the experiment was made.

# **Ohmic heating (OH)**

The schematic view of the Ohmic heating system is given in Figure 1. The OH system consists of power supply, isolated transformer, test cell, custom made microprocessor and electrodes. While the test cell was made of polyoxymethylene, the electrodes were made of stainless steel. First, 100 ml of sample was placed in the test cell and a T-type thermocouple was placed at its center. In order to prevent evaporation from the test cell during the heating process, a sealed cover was used. The model sugar solution was started to be heated at 15 °C and the heating process was terminated at 95 °C. Temperature history data was recorded every second with a custom-made microprocessor. In addition, current and voltage values were recorded in every second with the microprocessor. The 0-360 V variac system used in Ohmic heating allows precise adjustment of the desired voltage ( $\pm 0.5$  V). The voltage gradient used in the current study was determined as constant and its value was 13 V/cm. All trials were made in three replications.



Fig. 1. Schematic view of Ohmic heating (OH) system.

# Determination of Ohmic heating energy and Power values

In the OH process, using the current and voltage values obtained from the microprocessor, ohmic heating consumed energies (OHCE) were calculated with equation 1.

$$Q_{ohmic} = \sum (V \times I \times t).$$
<sup>[1]</sup>

Here, V (volt), I (amper) and t (second) symbols represent the voltage, current and time, respectively.

Depending on the energy value obtained and the duration of the ohmic heating process, the Power values were determined with equation 2 as unit of Watts.

$P_{ohmic} = -$	$\frac{Q_{ohmic}}{\Sigma t}$ .	[2]
$P_{ohmic} = -$	$\frac{Q_{ohmic}}{\Sigma t}$ .	[2]

Here, P (watt), Q (joule) and t (second) symbols represent the power value, energy value and time, respectively.

#### **Statistical Evaluation**

SPSS 16.0 (IBM, USA, 2007) package program was used for the statistical evaluation of the results. One-way analysis of variance (Post Hoc tests) was used to examine the effect of sugar concentration on total ohmic heating consumed energy and power value with the Totally Random Experiment Design. One-way analysis of variance Confidence level was taken as 95%.

# **RESULTS AND DISCUSSION**

The total consumed ohmic energy obtained in model sugar solutions with different sugar content is given in Figure 2. It has been determined that the total ohmic energy consumed for heating sugar solutions from 15 °C to 95 °C varies between 45.8-53 kJ. It was observed that the total ohmic energy consumed during the heating of the 40% TSSC sugar solution was 53 kJ. However, it was determined that this value decreased down to 45.8 kJ due to the decreasing sugar concentration. When the effect of sugar concentration was examined, there was a statistically negative significant difference at increasing sugar concentration (p < 0.05). In different studies, it has been reported that the heat transfer to the environment increases with the increase of the process time and therefore the energy consumed values increase (Icier, Yildiz, Sabanci, Cevik, & Cokgezme, 2017b). It has been reported that the increasing fat content negatively affects the processing time and the total energy consumed values at the cooking process with ohmic heating (Cevik & Icier, 2018). In the same study, it was stated that the process time was shortened with the decrease of the voltage gradient and as a result the efficiency value was reduced. In another study performed with ohmic evaporation process, it was reported that the process time was shortened with the decrease of the voltage gradient and the total energy consumed value decreased (Icier et al., 2017b). In the present study, especially due to the increase in the concentration of sugar solution, molecular mobility was restricted, and the heating time was increased. Therefore, it was determined that increasing sugar concentration had an effect on the total ohmic energy consumed. The average power value of the system during the heating of the model solution from 15 °C to 95 °C is given in Figure 2. The power value obtained during the OH process varied between 161.8-72.8 W. At the end of OH process, the average power values of the solutions with 10%, 20%, 30% and 40% sugar concentrations were determined to be 161.8 W, 134.4 W, 97.7 W and 72.8 W, respectively. Contrary to the total energy consumed values, it was determined that as the sugar concentration increased, the average power value decreased. The increased percentage of sugar content in the ohmic heating process resulted in increased processing time. The increase in the percentage of sugar in the solution used restricts the molecular mobility and therefore increases the processing time. For this reason, the power value was negatively affected due to the negative relationship between time and power (Equation 2). It has been determined that the 40% sugar concentration limits the molecular mobility and the long processing time affect the power value negatively. It has been reported that the increasing voltage gradient shortens the process time and affects the power value negatively at ohmic heating evaporation processes.



Fig. 2: The total consumed ohmic energy and the power value obtained in model sugar solutions with different sugar content

# CONCLUSION

In the ohmic heating assisted heating system, the total ohmic energy consumed and average power values were determined during the heating of the model solution from 15 °C to 95 °C. It was determined that the total consumed power value varied between 45.8-53 kJ for 10-40% sugar solutions, while the average power value varied between 161.8-72.8 W. It has been determined that the increase in the sugar content in the solution used has increased the processing time due to the limitation of molecular mobility and this negatively affects the power value. As a result, the sugar concentration in the ohmic heating process had an effect on the total consumed energy and power values.

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# IS THERE A REBOUND EFFECT AFTER ENERGY RETROFIT OF MULTI-APARTMENT BUILDING? EVIDENCE FROM KAUNAS CITY, LITHUANIA

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#### ABSTRACT

In Lithuania, multi-apartment buildings are significant heating energy consumers. As in many post-Soviet countries, there are many old and energetically inefficient multi-apartment buildings with a significant energy efficiency potential through retrofit. It can help residents save on heating energy costs, reduce environmentally harmful greenhouse gas emissions and improve the overall image of the city.

Scientific literature suggests that actual energy savings depend not only on technical measures implemented but also on behavioural and other side factors that may lead to a rebound effect when energy efficiency increase is followed by increased use of energy services. In this study, the direct rebound effect after the energy retrofit of multi-apartment buildings is investigated. A database of 66 already renovated during 2014-2018 years period multi-apartment buildings in Kaunas city, Lithuania was created by combining the data from various sources. Heating energy consumption data were recalculated according to annual heating degree days to ensure comparability. The analysis has shown that there are no significant rebound effects in most of the renovated multi-apartment buildings in Kaunas. Among other factors, this can be explained by the relatively narrow range of comfortable indoor temperatures and successfully implemented multi-apartment buildings energy retrofit.

Keywords: heating energy, rebound effect, multi-apartment buildings retrofit, Kaunas city.

## **INTRODUCTION**

There are 38 thousand multi-apartment buildings in Lithuania, and the vast majority of them (35 thousand units) were built before 1993 [1]. They were built following low-quality standards and using poor construction practices. In many cases, they have not been adequately maintained for a long time. As a result, most Lithuanian multi-apartment buildings fail to be energy-efficient. This leads to increased expenditures on heating. The residents of apartments in energy-inefficient buildings may have to pay 2-3 times or sometimes even ten times more for heat compared to heating expenditures of newly built and energetically efficient multi-apartment buildings residents [2].

Estimates of the Lithuanian Association of Heat Suppliers [3] show that even minor energy retrofit of a multi-apartment building (i.e., the arrangement of the engineering systems) may reduce the payments for heating per apartment on average by about 15 Eur/month (this would be approximately 90 Eur during the entire heating season). The effect of complete energy retrofit would be even more considerable as heat consumption may be reduced more than three times based on energy audit data. Although there is a substantial technical energy efficiency potential, actual energy savings also depend on additional factors. Thus, an accurate estimation of the realisable energy-saving potential must take into account implicit factors, such as the rebound effect [4], especially direct rebound. The direct rebound effect in the household sector can be observed when multi-apartment buildings energy retrofit reduces the effective cost of the heating service, but increased consumption due to many factors increases them again. The rebound effect is also important in shaping the nation's energy policy, as its size can determine the extent to which energy efficiency improvements can achieve the intended goals [5]. Rebound effects in Lithuania are rarely analysed despite the claims that the rebound effect for domestic energy services consumption in Lithuania is highest in Europe as energy consumption growth is much more significant than energy efficiency improvements [6]. It should be noted that the rebound effect's statistical estimations may be misleading if highly aggregated data are used since the aggregation effects may be treated as rebound evidence. Therefore, more attention has to be paid to individual efficiency programs and individual energy consumption changes before generalising.

The multi-apartment building energy retrofit program can be considered as the largest program oriented towards household energy consumption in Lithuania. The analysis of rebound effects related to the energy retrofit of multi-apartment buildings presented in this paper focuses on the Kaunas case, which may be considered as representative in the Lithuanian context. Average climatic conditions due to the location in the middle of the country, energy retrofit progress rate close to Lithuanian average, and other factors make this case relevant for the description of the overall Lithuanian situation.

In this article, a dataset of 66 of multi-apartment building energy retrofit cases is analysed observing energy consumption changes over time to examine the rebound effect's existence. This article is separated into different sections. Section 2 overviews multi-apartment buildings modernisation process in Lithuania, Section 3 analyses rebound effect in residential sector, Section 4 presents research methodology, Section 5 discusses research results, and Section 6 lists the main conclusions.

# AN OVERVIEW OF MULTI-APARTMENT BUILDING MODERNISATION PROCESS IN LITHUANIA

To increase energy efficiency and contribute to the development of reliable and efficient energy, the government is actively promoting multi-apartment building retrofits in the country. The current program foresees a set of measures to promote energy retrofit of multi-apartment buildings. It includes reconstruction or replacement of heating and hot water systems, roof insulation and etc.

According to Housing Energy Efficiency Agency (BETA) [7], 3126 thousand old multiapartment buildings were successfully renovated in Lithuania since 2004 when Lithuanian housing strategy was approved, and old multi-apartment buildings retrofit processes began.





There are considerable differences in renovation pace among areas of the country. As shown in Fig. 1, the share of renovated multi-apartment buildings in the total multi-apartment building stock varies from 4,4 % to 17,8 %, with Alytus county leading in this process (282 renovated multi-apartment buildings out of 1582). Various reasons explain these differences, starting from housing stock structure and ending with national government support for certain municipalities and local administrative capabilities. Residents' expectations about future savings also play a considerable role in the individual decision-making process and, consequently, in the pace of the overall modernisation program. Therefore, the research that sheds more light on building modernisation can contribute to better informed and rational decisions.

Out of all ten Lithuanian counties, Kaunas county is currently the renovation leader by absolute numbers, with 580 already renovated multi-apartment buildings. The rather low relative share of renovated multi-apartment buildings (7.3 %) may also be related to the specific housing stock features in Kaunas: due to historical reasons, a significant share of multi-apartment buildings consist of very small buildings (3-4 apartments per building) and tend not to participate in a state-wide modernisation program. In this study, the main attention is paid to larger buildings with 3 to 13 floors and 3 to 100 apartments.

## **REBOUND EFFECTS IN RESIDENTIAL ENERGY CONSUMPTION**

Li and Lin defines rebound effect as "the lost part of energy conservation which is offset by increased energy consumption" [8]. There are different types of rebound effect: direct, indirect and economy wide [9]. One of the most important of them is direct rebound effect, as it is directly related to the efficiency of multi-apartment buildings retrofit.

Han, Shi, Yang and Wang [10] divided direct rebound effect in energy into these four categories:

- The same consumer for the same goods or services;
- Different consumers for the same goods or services;
- The same consumer for different goods or services;
- Different consumers for different goods or services.

The most vivid rebounds fall to the first category that is also the most likely for heating after energy retrofit. It might be well that low energy efficiency level is related to insufficient heating due to either technical or income limitations. Other categories of rebound effect are less strictly defined due to possible overlapping links, and their unambiguous identification is far more complicated.

The factors causing the rebound effect in household heating energy consumption are extensively studied in the literature. Several of them were singled out after an analysis of the scientific literature:

• **Heating energy prices.** Energy efficiency improvements lead to reduced energy consumption and reduced expenses for energy. As a result, residence buildings tend to consume more. [11]. Energy efficiency improvements should reduce energy consumption and increase cost per unit of energy to cover all fixed costs. Thus, in most of the cases, energy price increase should stipulate further reduction of energy consumption. However, heat price fluctuations may be caused by other reasons, for

example market developments or structural changes in the energy sector, as was the case with the shift to biomass in Lithuanian district heating.

- **Households income.** The lower rebound effect is recorded when high income is received and then there is less sensitivity to energy service prices [12]. In other words, if the income does not restrict energy consumption before the implementation of energy efficiency measures, likely, that their implementation would not cause a significant increase in the consumption of energy services afterwards.
- **Households behaviour.** The larger change in consumption can be explained by household behavioural factor such as time spent at home, comfort preferences and others. Behavioural factors are usually not included in the predictions [13]; Behavioral factors may be determined by energy retrofits (increased comfort provides an incentive to spend more time at home) or related to external factors such as lockdowns due to pandemics.
- **Climate change.** Warmer winters imply less need for thermal insulation [14] which means that a rebound effect would also be smaller. To extract a "pure "rebound effect, climate-corrected energy consumption values have to be used.

## METHODOLOGY

Overall, there are 239 already renovated multi-apartment buildings in Kaunas city. A database with 66 of them retrofitted during 2014-2018 years period was created by using AB Kauno energija, SPSC (centre of construction products certification) and BETA (Housing Energy Efficiency Agency) data.

As stressed in the previous section, the rebound effect is observed in the context of various other changes in the system analysed. However, the "pure" rebound effect is mainly related to the reduced expenses due to energy savings and increased availability of funds to be used for energy needs. To isolate additional factors, actual energy consumption data have to be corrected.

Heat consumption during a year heavily depends on weather conditions that particular year. If corrections are not made, increased heat consumption due to colder winter might be treated as the rebound effect. To avoid this misinterpretation, heat consumption data were corrected using heating degree days (HDD). "Heating degree day describes the demand for energy needed to heat buildings" [15]. The following equation was used to calculate corrected heat consumption values:

corrected consumption<sub>t</sub> = 
$$\left(\frac{HDD_s}{HDD_T}\right) \times actual consumption_t$$
,

there  $HDD_s$  is normative heating degree days,  $HDD_t$  is average yearly heating degree days during 2011-2019 period and *actual*<sub>t</sub> is heat consumption in the year t.

To determine the direct rebound effect the heating energy consumption corrected by heating degree days (HDD) for each of the multi-apartment building was observed in up to the first five years after retrofit implementation depending on the year in which the retrofit was completed. This reflects an assumption that residents may increase energy consumption after realising actual energy savings (benefits they obtain) during the first year after the retrofit.

Heating energy consumption in the first five years after retrofit was ranked on a scale of 1 to 5, where the higher number means lower heating energy consumption.

The rebound effect was identified by using two methods.

**Method number 1:** assuming that in all the years following retrofit, the multi-apartment building consumes more heating energy than during the first year after retrofit.

**Method number 2:** assuming that the average heating energy consumption for the whole of the following year is significantly higher than the consumption during the first year after multi-apartment buildings retrofit.

#### RESULTS

One can intuitively assume that heat consumption should decrease significantly after retrofit implementation. In order to check whether there are exceptions in the case of Kaunas city, the heat consumption in the first year after renovation and before the renovation was compared. A comparison is given in the scatter plot below. However, the model presented in the graph is not very accurate due to the relatively low level of the coefficient of determination equal to 0,397.



Fig. 2. Heating energy consumption during year of the retrofit end and first year after retrofit  $(kWh/m^2)$ 

It was noticed that already in the first year after the renovation the heat energy consumption decreased proportionally compared to the year before the renovation, therefore there are no exceptions in Kaunas city.

Examining the rebound effect in the first five years after renovation, the number of multiapartment buildings is different and varies every year, because five years have not yet passed since the end of some of their renovation. Assuming that in all the years following the retrofit of the multi-apartment building, the multi-apartment building consume more heating energy than during the first year after retrofit (method number 1) and assuming that the average heating energy consumption for the whole of the following year is significantly higher than the consumption during the first year after multi-apartment buildings retrofit (method number 2) the rebound effect in the first five years after renovation was examined. The number of multi-apartment buildings is different and varies every year, because five years have not yet passed since the end of some of their renovation.



Fig. 3. Observed rebound effect

According to both rebound effect calculation methods, the rebound effect in the renovated Kaunas city multi-apartment buildings is observed in rare cases. The maximum rebound effect equal to 9.09 % was observed with the first method, and with the second method it is only equal to 6.06 %.

The weak rebound effect is also revealed by the studied dynamics of heat energy consumption in percent.



Fig. 4. Changes in heating energy consumption

Energy consumption decreased in the majority of buildings. It is difficult to identify the reasons of energy rebound in the remaining buildings. For further analysis to determine the reasons for the increase in heat energy consumption after retrofit implementation, the behaviour of the residents could be analysed along with the analysis of technical features.

# CONCLUSIONS

Current building modernisation progress with less than ten percent of the stock retrofitted over the last sixteen years is far from sufficient, taking into account ambitious decarbonisation and energy efficiency targets. An analysis of rebound effects in building modernisation contributes to better-informed decisions and evidence-based energy policy.

Identification and evaluation of rebound effects require side factors to be isolated. Energy consumption recalculations based on heating degree days enables a fair inter-temporal comparison of energy consumption in different years. Consequently, this allows the identification of rebound effects after building energy retrofit.

The analysis has shown that there is no significant rebound effect in renovated multi-apartment houses in Kaunas. This can be partially explained by the nature of district heating. First, before retrofits, residents typically fail to have a real possibility to reduce their energy heating consumption. Therefore, it is less related to income constraints, even in lower-income households. Second, the indoor temperature that ensures the highest comfort level falls to a relatively narrow range. Thus, the residents have limited motivation to increase temperature despite the insignificancy of additional heating expenditures after the retrofit. Finally, energy efficiency investment not necessarily reduces total energy-related expenses: although heating expenses decrease, additional payments are related to the cost of the energy retrofit. If they are significant, the changes in the household budget may be modest.

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# QUANTITATIVE ASSESSMENT OF MEASURES TO IMPROVE THE EFFICIENCY OF OPERATION OF ELECTRICAL DISTRIBUTION NETWORKS UNDER THE CONDITIONS OF THE ELECTRICITY MARKET IN UKRAINE

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#### ABSTRACT

Distribution electricity networks (DENs) are an important element in the power system, serving as a link between the generation system via feeder networks and electricity consumers. DENs are characterized by long lines, a significant number of substations, a branched and complex structure, and high requirements for reliability of power supply and quality of electricity at consumers. The role of DENs in ensuring the reliability of electricity supply to consumers is increasing in terms of the introduction of the new model of competitive electricity market in Ukraine. The assessment of the technical condition and reliability indicators of DENs of Ukraine performed in the article confirmed the need to develop and implement measures to improve the efficiency of their functioning.

The groups of technical and organizational measures to improve the efficiency of DENs functioning were developed by the authors taking into account the current situation in the electricity market of Ukraine, load characteristics, technical condition, features of the structure and functioning of the DENs. These measures take into account the possibility of attracting modern methods and technologies, scientific and technical means for a comprehensive approach to solving the problem under study.

The main trends in the development of the energy sector have been taken into account by the authors in formulating options to improve the functioning of the DEN: Measures to improve operational efficiency and ensure the required level of operational reliability have been identified for urban, industrial and rural DENs using the proposed criterion. The analysis of the results shows that there is no single solution to this problem. The justification for measures to improve efficiency of electricity network operation should be given on an individual basis for each specific DENs.

This paper presents a comprehensive technical and economic criterion, which was developed by the authors to quantitatively assess the feasibility of applying the proposed measures to improve the functioning of the DENs. The maximum profit of the energy distribution system as one of the participants of the electricity market is used as this criterion. Requirements for ensuring the DENs mode, reliability of power supply to consumers and quality of electric power are considered as limitations. The value of the developed integrated technical and economic criterion was  $0.61 \div 0.97$  for urban,  $0.63 \div 0.97$  for industrial and  $0.58 \div 0.98$  for rural DENs under study.

**Keywords**: distribution electric networks, electricity market, economic criterion, profit, renewable energy sources, regime, reliability, electric energy quality

#### **INTRODUCTION**

Distribution electric networks (DENs) are an important element in the electric power system, performing communication between the generation system through the supply network and electricity consumers. A new model of electricity market is introduced in Ukraine. The power supply system is interconnected with the power supply system operator in accordance with a new model, due to the safety of the current power supply, ensuring the requirements harmonization of electricity consumers with the current situation in the electricity market. This indicates that the quality, safety and DENs operation reliability determine the efficiency of the whole Ukraine unified energy system (UES).

Maintaining the required level of DENs operation reliability requires the certain DENs technical status provision, which involves the development and implementation of technical and organizational measures to improve the DENs functioning efficiency, taking into account the development state and DENs functioning peculiarities, current situation in the electricity market and current trends in the development of electricity transmission engineering and technology. Thus, identifying the most feasible measures to improve the DENs functioning efficiency in the electricity market is a complex and at the same time very important practical task for Ukraine's energy sector.

Much attention has been paid to the issues of improving the DENs operation by both scientists and employees in energy systems around the world. Among the most significant are the studies on circuits optimization and electricity losses reduction in electric networks [1-4], new technologies introduction to increase the efficiency of electricity transmission and distribution [5-9], study of the modern DENs operation modes peculiarities [10- 13], improvement of electricity quality in DENs [14-17]. However, the issue of quantifying measures to improve the DENs functioning efficiency is not well developed to date, despite the considerable publications volume.

The measures evaluation to improve the DENs functioning efficiency, taking into account the network structure peculiarities, the consumers functioning and the current situation in the electricity market, was the purpose of the conducted research.

# TECHNICAL STATE CHARACTERISTICS OF THE DISTRIBUTION ELECTRIC NETWORKS IN UKRAINE

The current electricity distribution system in Ukraine is located in the territory of 27 regions and includes more than 1 million km overhead power lines and cable power lines of 0.4 - 150 kV power transmission and over 200 thousand 6 - 150 kV transformer substations [18]. The block diagram of the electricity distribution system in Ukraine is presented in Fig. 1.



Fig. 1. The block diagram of the electricity distribution system in Ukraine

Each electricity distribution system is serviced by the distribution system operator, which in Ukraine is created through on-base discharge from former power companies. Main tasks of the distribution system operator are to ensure fair, transparent and non-discriminatory access to information for all participants in the electricity market, as well as to maintain the necessary technical condition, to provide the service of consumers' electrical installations connection to the distribution system in accordance with the distribution system code [19] and to organize the management of distribution system modes according to [20]. The operator also plans the distribution system development taking into account energy efficiency measures and the main directions of the country's energy industry development strategy [21].

Distribution systems have construction features, depending on the nature and customers territorial location they serve. The electricity consumption structure in Ukraine in the consumer groups context is presented in Fig. 2 according to the National Power Company Ukrenergo [22].



Fig. 2. Electricity consumption structure in Ukraine for 2019

The analysis shows that the structure of electricity consumption in Ukraine is quantitatively dominated by household consumers and utility consumers, located and territories of settlements. A significant share in the electricity consumption is also made by industrial consumers who are located in the settlements territory or in the immediate vicinity of them.

DENs are characterized by a large length of lines, a significant number of substations, a branched and complex structure, high requirements for the power supply reliability and the quality of electricity among consumers.

At the same time, DENs have the structural construction specifics, operation, operational reliability and mode control, depending on which particular electricity consumers prevail in the composition. DENs can be conditionally allocated as urban, industrial and agricultural. So, urban DENs are characterized by a high load density. They are performed mainly by cable power lines (PLs) using a rated voltage of 10 (6) and 0.4 kV. Distribution points and two-transformer transformer substations (TS) are used quite often in the structure, loopback networks radial and double-beam prevail. Industrial networks have a small length and high load density, 110/10 kV overhead lines for power supply of deep input substations and cable lines for shop transformer substations power supply and intra-shop networks are used, double-beam, radial and backbone network circuits prevail. Agricultural networks are characterized by their considerable length and low load density. Overhead power lines with a nominal voltage of 110, 35, 10 (6) and 0.4 kV are used, backbon, radial and loopback networks prevail. The DENs characteristics by predominant consumers types are presented in Table 1.

The sign name	DENs type			
The sign name	Urban	Industrial	Agricultural	
Load density	high	medium, high	low	
DENs length	small	small	Much	
Power lines type	cable power lines	overhead power	overhead power lines	
		lines and cable		
		power lines		
DEN configuration	double-beam,	double-beam,	backbone, radial,	
	radial, loopback	radial, backbone	loopback	
Voltage	10(6), 0.4 kV	110, 10(6), 0.4 kV	110, 35, 10(6), 0.4 kV	

Table 1. The DENs characteristics by predominant consumers types

The current DENs technical status in Ukraine is characterized by the following factors:

- significant physical and moral deterioration of the equipment (DENs average age of infrastructure is more than 30 years, and the total wear rate exceeds 65%, which is shown in Fig. 3), which can lead to emergencies and disruption of the electricity supply to consumers;

- inefficient DENs configuration, which is a consequence of the gradual development and reconstruction, it manifests itself in a considerable length of transmission lines, as well as in the sub-optimal electrical networks structure, which leads to an increase in voltage and power losses, a decrease in the quality of electricity in such DENs;

- measurement systems imperfection, relay protection and operational control, low automation level, which reduces the modern technologies introduction efficiency, equipment, devices and means for ensuring efficient and reliable electrical networks and systems functioning;

- low capacity of transmission line, which causes difficulties in the network further development, complicates the new subscribers connection (both consumers and distributed generation sources);

- increase in the distributed number of generation sources in the DENs, which have an unstable power output schedule, which leads to an imbalance of the generating capacities structure and reduces the regulating efficiency of electric networks and systems modes;





- unstable operation and emergencies, which leads to a decrease in the quality of electricity supply to consumers and is expressed in an unsatisfactory level of the average duration index (SAIDI) and the index of system shutdowns (SAIFI) for DENs in Ukraine (the

power interruptions duration in Ukraine ranges from 580 to 870 minutes (Fig. 4), while in EU countries - up to 40 minutes [23]);

- low efficiency of electricity transmission, which leads to an increase in the electricity cost in the Ukrainian UES.



Fig. 4. Dynamics of reliability indicators for DENs in Ukraine

The DENs role in ensuring the reliability of power supply to consumers is growing in the new model introduction context of a competitive electricity market in Ukraine. The performed assessment of the DEN technical condition and reliability indicators confirmed the need for the development and implementation of measures to increase the DENs functioning efficiency.

It should be noted that the mechanism of new liberalized market in Ukraine provides more opportunities for DENs to address the implementing measures issues to improve the operation efficiency and improve the quality of electricity supply to consumers.

# WAYS TO INCREASE THE FUNCTIONING EFFICIENCY OF THE DISTRIBUTION ELECTRIC NETWORKS IN UKRAINE IN THE ELECTRICITY MARKET CONDITION

The technical and organizational measures groups to increase the DENs functioning efficiency were developed taking into account the current situation in Ukraine electricity market, load characteristics, technical condition, structural and DENs functioning features. These measures take into account the attracting modern methods and technologies possibilities, scientific and technical means for an integrated approach solving this problem.

The main trends in the energy industry development in Ukraine were taken into account when drawing up options for increasing the DENs functioning efficiency:

- an increase in the number of distributed generation sources on DENs, which are increasingly being renewable energy sources (RESs), is observed in current conditions;

- the using energy storage systems (ESSs) in RESs is appropriate to increase the RESs generation stability;

- the using intellectual equipment, automated electricity metering systems and DENs operating modes control for the implementation of subsequent Smart Grid technologies is one of the Ukrainian energy strategy priority areas;

- giving advantage to innovative technical solutions.

The main measures for improving the DENs efficiency can be divided into technical and organizational, the list of which is presented in Fig. 5.



Fig. 5. Classification of reliability measures to improve the DENs efficiency

In order to formulate a list of measures, it is advisable to choose the measures from the general list that are most economically and technically feasible for the electricity networks under consideration for each specific task. The DENs characteristics, the source and investment size for the implementation of practical measures to improve the DENs efficiency should be taken into account.

# CRITERION FOR MEASURES EVALUATION FOR INCREASING THE FUNCTIONING EFFICIENCY OF UKRAINE DISTRIBUTION ELECTRIC NETWORKS IN THE ELECTRICITY MARKET CONDITIONS

A comprehensive technical and economic criterion was developed to quantify the feasibility of applying the proposed measures to increase the DENs functioning efficiency. The maximum energy distribution system profit as one of the participants in the electric energy market is used as this criterion [24]:

$$K_{ef}(x) = \sum_{m=1}^{M} w_{R_m} \cdot R_m(x) + w_C \cdot C(x) + w_K \cdot K(x) + w_{\eta_{ESS}} \cdot \eta_{ESS}(x),$$
(1)

where x – the number of measures group to increase the DENs functioning reliability, which is characterized by a network parameters vector;  $R_m(x)$  – DENs reliability index (SAIDI, SAIFI, MAIFI, ENS, etc.), the value of which is determined in accordance with [25]; M – the quantity of DENs reliability indices, which are taken into account in the calculation; C(x) – total costs of measures in the electricity distribution system to increase the DENs functioning reliability; K(x) – the amount of compensation to consumers for guaranteed quality standards violation for the provision of electricity services, which the distribution system operators counts and provides the consumer in accordance with [26];  $\eta_{ESS}(x)$  – efficiency of the ESSs used;  $w_{R_m}$ ,  $w_C$ ,  $w_K$ ,  $w_{\eta_{ESS}}$ – weight coefficients that take into account the importance of the DENs reliability indices  $R_m(x)$ , the total cost of measures to increase the reliability of C(x) and compensation to consumers for guaranteed quality standards violation for the provision of electricity services K(x) according to the electricity market current state, as well as the efficiency of the ESSs used.

Requirements for ensuring the DENs regime, the power supply to consumers reliability and the electric energy quality are considered as limitations [24]:

$$\begin{aligned} SAIDI(x) &\leq SAIDI_{max}, \quad SAIFI(x) &\leq SAIFI_{max}, \\ MAIFI(x) &\leq MAIFI_{max}, \quad ENS(x) &\leq ENS_{max}, \\ P_{EEQ}(x) &\leq P_{EEQ_{max}}, \qquad P_{mode}(x) &\leq P_{mode_{max}}, \end{aligned}$$
(2)

where  $SAIDI_{max}$ ,  $SAIFI_{max}$ ,  $MAIFI_{max}$ ,  $ENS_{max}$  – the maximum values of the reliability indexes for distribution electric networks, which correspond to the required level of electricity supply services;  $P_{EEQ_{max}}$  – maximum permissible values of electric energy quality indicators;  $P_{mode_{max}}$  – maximum allowable DENs mode parameters values (voltages at the network nodes, currents in the lines, etc.).

To determine the expedient measures to increase the DENs reliability from the list of calculated efficiency criteria, determine the minimum:

$$K_{ef}(x) \rightarrow min$$
. (3)

# ANALYSIS OF MEASURES FOR INCREASING THE FUNCTIONING EFFICIENCY OF UKRAINE DISTRIBUTION ELECTRIC NETWORKS IN THE ELECTRICITY MARKET CONDITIONS

Measures to increase the DENs functioning efficiency and ensure the operational reliability required level were identified for more than 30 urban, industrial and rural distribution zones using the proposed criterion. The most appropriate of the measures considered were selected using the developed criterion (1). The calculation results are presented in Table 2.

An analysis of results showed that there is no single solution to this problem. The justification of measures to increase the functioning efficiency should be given individually for each specific DEN.

The number		Efficiency criteria for DENs $K_{ef}(x)$ ,		
of measures	The characteristic of	rel. units		
increase DENs functioning efficiency x	measures to improve DENs functioning efficiency	Urban	Industrial	Agricultural
1	Intellectual equipment installation	0.73-0.85	0.71-0.83	0.79-0.88
2	Conversion of the electrical network from 10 kV to 20 kV using protected wires	0.89-0,91	0.81-0.92	0.69-0.86
3	Protected wires using	0.88-0.96	0.78-0.89	0.62-0.78
4	Reclosers installation	0.65-0.77	0.86-0.97	0.58-0.79
5	Distributed generation implementation, relay protection mode change	0.76-0.97	0.88-0.95	0.67-0.83
6	ESSs implementation	0.73-0.88	0.67-0.84	0.62-0.82
7	Distributed generation implementation, ESSs implementation	0.61-0.84	0.63-0.82	0.58-0.78
8	Electricity metering systems improvement	0.91-0.95	0.89-0.97	0.92-0.98

Table 2. Evaluation of measures to improve the DENs functioning efficiency

## CONCLUSIONS

The performed analysis showed that the unsatisfactory technical state of modern DENs in Ukraine significantly reduces the efficiency and reliability of both DENs and the Ukrainian UES as a whole.

In order to increase the reliability of DENs functioning for each of the regional electricity distribution systems, it is necessary to develop and implement a number of organizational and technical measures that will update the structure and configuration of networks, and will contribute to the electrical networks intellectualization development.

A criterion of technical and economic efficiency, which takes into account the DENs characteristics and technical status, current state features of the electricity market and the charging consumers specifics for quality standards violations in Ukraine, was developed to substantiate the applying measures feasibility to improve the DENs efficiency.

Projects implementation to improve the DENs efficiency and reliability requires careful evaluation and significant investment, but their implementation is a prerequisite for the further development of Ukraine's energy sector.

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# INVESTIGATION ON THERMAL MANAGEMENT PERFORMANCE OF PCM/GRAPHITE MATRIX FOR LI-ION BATTERY CELL: PRELIMINARY RESULTS

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#### ABSTRACT

An experimental study is carried out to investigate the thermal behaviour of Li-ion cell following the of phase change material (PCM)/graphite matrix, which is a passive thermal management method. The PCM (RT42, paraffin/ organic), is impregnated to the graphite matrix, with the bulk density of 75 g/L. Cooling performance of the single cell is reported at 2.5C discharge rates for PCM/graphite matrix and also air cooling, comparatively. The time-history of temperature measurements, thermal camera imaging, and voltage-capacity curve are obtained to reveal the thermal performance of PCM/graphite matrix in detail. The results illustrate that PCM/Graphite Matrix has a significant effect on the phase change heat transfer, operating temperature, and available capacity comparatively to air cooling. Effective thermal conductivity which enhances the heat transfer rate is shown to increase 40 times compared to that of pure paraffin. Operating temperature and temperature gradient throughout li-ion surface decrease by 34 % and 80 % compared to natural air cooling. Utilized capacity is increased by 16 % compared to natural air cooling. Uniform melting behaviour is observed based on highly conductive abundant thermal paths for PCM/graphite matrix. It is also disclosed that heat transfer takes place by dominant conduction for the PCM/graphite matrix.

Keywords: Thermal management, cooling, li-ion, battery, pcm, graphite, expanded graphite

#### **INTRODUCTION**

The progress of electric vehicles (EVs) in recent decades is viewed as a considerable potential to minimize environmental pollution depends on combustion-related emission/greenhouse gases and energy problems [1]. The key parameter of electric vehicles is to produce the promising energy storage technology which can support high driving mileage and fast acceleration. Among battery technologies, li-ion batteries are the most promising power sources with no memory effect, lower self-discharge, lower mass density, higher energy density and stable performance for EVs and also other applications such as electronics, robotics, aeronautics and space, renewable energy sources, etc. One of the major hindrance regarding the li-ion is temperature-caused degradation. There are two main temperature concerns about li-ion batteries: unacceptable operating temperature, low-temperature uniformity. Adverse effects of temperature can be categorized as high temperature-caused performance degradation, thermal runaway, temperature maldistribution, and low-temperature behaviour. To obtain the optimum performance, the operating temperature of the li-ion battery needs to be kept within an acceptable range of -20 °C - 60 °C /15 °C - 35 °C. Besides, the maximum temperature difference among cells in the battery pack is desired to be less than 5 °C. Therefore, a well-

designed thermal management system is required to ensure better battery performance and safety during charge/discharges [2-6].

A battery thermal management system (BTMS) can be categorized into active, and passive. Among these methods, BTMS through phase change material (PCM, solid/liquid) of passive method is an attractive way due to high energy storage capability and isothermally process. Besides, a PCM-based battery thermal management system ensures minimizing the complexity and providing weight, volume, power consumption, noise, and esthetic savings. Therefore, many studies have been conducted by researchers on PCM-based BTMS during the last decade. Nevertheless, thermal conductivity and leakage issues of PCM-based thermal energy storage systems including solid/liquid phase transition and organic/paraffin type are two main bottlenecks restricting usage of PCM-based technology. Thermal conductivity affects the thermal diffusivity ( $\alpha$ , m2/s) negatively. Lower thermal diffusivity means heat transfer and phase transition slowly. Besides, during melting (solid-liquid), form stable is not provided. So, it requires encapsulation of PCM. This weakness of material depending on its nature can be improved using different methods investigating by researchers including increasing the heat transfer surface area [7], geometric optimization [8], dispersing particles (carbon, nano, etc.) with high thermal conductivity [9], insertion of metal matrix [10], impregnated graphite foam/matrix [11], encapsulation [12].

Among the heat transfer enhancement strategies, graphite matrix has become one of the topics of increased research interest with its potential of improving the thermal conductivity of PCM and phase change heat transfer process and preventing leakage issue. Graphite matrix ensures these advantages depending on high porosity reaching 95 %, low density, high thermal conductivity, good mechanical properties, compatibility with surfaces proving high ratio of surface area to volume, and chemically non-reactive nature. Also, a graphite matrix is a porous medium that provides an encapsulation of PCM. The phase change material is impregnated to the graphite matrix by capillarity and surface tension phenomena. Impregnation encapsulation is one of the shape-stabilized PCMs methods which allows phase change materials to retain solid phase form during the solid-liquid phase transition and does not allow any leakage. Therefore, shape-stabilized PCM is one of the effective ways of encapsulation [12].

Recent investigations on the thermal management of li-ion batteries for PCM/graphite matrix are given as follows. Mills et al. [13] first reported (within the authors' knowledge) an expanded graphite matrix for battery cooling. They studied thermal conductivity, paraffin mass fraction, and latent heat of fusion of PCM/graphite matrix composite samples. They revealed the potential of the PCM composite for passive thermal management systems. Kızılel et al. [14] investigated the effect of the PCM/graphite matrix thermal management systems over conventional active cooling systems. The results showed that the surface temperature of the cells was kept at lower temperatures when PCM was used. A numerical study was conducted to investigate the cooling performance of PCM/graphite matrix structure for a cylindrical battery pack by the same research group Kizilel et al. [15]. The PCM/graphite matrix helped the battery to achieve a more uniform distribution and to avoid the propagation of a thermal runaway from one cell to the entire pack. Somasundaram et al. [16] carried out a numerical study by using a two-dimensional, transient mathematical model comprising conservation of charges, species, and energy for cylindrical li-ion battery under different discharge rates. The results showed that lower temperature measurements were observed with a PCM/graphite. The thermal performance of composite PCM-based BTMS was performed by Greco et al. [17]. They observed that the relation between latent heat and thermal conductivity was important. The authors also presented that the bulk density of graphite-matrix was a critical parameter for optimizing the PCM/graphite matrix BTMS. Swhietzer et al. [18] developed a lumped (0-D) numerical model for simulating the thermal response of a lithium-ion battery pack with a PCM/graphite matrix. Lin et al. [19] used expanded graphite matrix and graphite sheets to

enhance the low thermal conductivity of PCM (paraffin/EG). The results showed that the uniform temperature distribution of the batteries was provided by PCM. Wilke et al. [20] investigated the effect of the solid-liquid phase change composite (PCM/graphite matrix) on the thermal runaway for a single cell. Experimental results show that the use of PCM composite reduced the maximum temperature of adjacent cells by nearly 60 °C and prevented thermal runaway from propagating between the cells after nail penetration. Jiang et al. [21] carried out an experimental and numerical study on composite PCM (EG/paraffin powder)-based BTMS. The PCM was enhanced with EG and was packed in aluminum tubes to further enhance the thermal conductivity. The tube-shell battery module exhibited high efficiency of heat dissipation and the rise of temperature was reduced significantly, but the temperature difference across the whole battery pack was near 12 °C. Mallow et al. [22] studied two enhancement materials including aluminum and graphite foams, and the enhancement materials saturated with PCM. The result indicated that the thermal charging enhancement of graphite foams is superior to that of aluminum foams. He et al. [23] developed CPCM by introducing a binary thermal conductive framework of EG/copper foam (CF) for BTMS. The results showed that the composite PCM-based battery pack with EG/CF (CPCM-EG/CF) achieves much better cooling and uniform temperature distribution than those without EG/CF or CF.

Because the li-ion battery is promising and updated technology in terms of an anode, cathode, electrolyte, etc., researches on thermal management are renewed by authors. From the cited literature, there are some studies on PCM/graphite matrix or foam for different li-ion chemistries or simulative batteries under various loading conditions. However, it is shown clearly that the researches are limited. Hence, the motivation of this investigation is to evaluate the effect of the melting phenomenon and porous media of PCM/graphite matrix on the heat dissipation process for battery thermal management, which is essential for better performance and safety requirements. To evaluate the melting behaviour and thermal energy storage performance, the time history of temperature, thermal camera images of PCM/graphite matrix are utilized under 2.5C discharge rate. The electrical performance of the li-ion is also given via the voltage-capacity variation and power/energy capacity. Experimental results presented compared with air cooling. The results given in this paper are preliminary results of an ongoing project.

## **EXPERIMENTAL STUDY**

## Heat storage material and graphite matrix

Paraffin of RT42 supplied from Rubitherm is used as phase change material in this study. Paraffin is known to be an attractive material with its advantages including, no phase segregation, chemical/physical/thermal stability, good compatibility with other materials, and non-reactivity, safe and high latent heat of fusion. The thermophysical properties of the paraffin and paraffin/graphite are presented in Table 1. Heat flow as a function of the temperature of pure paraffin and paraffin/graphite is measured in Fig.1 by DSC analysis (Hitachi-DSC 7020).

Properties	Paraffin	PCM/Graphite Matrix
	(Rubitherm-RT42)	
Melting temperature (°C)	41.4	35.5
Latent heat (kJ/kg)	162	148
Density (kg/m3) (solid)	880	730
Thermal conductivity	0.2	8
(W/m.K)		

Table 1. Thermo-physical properties of the paraffin and PCM/graphite matrix



Fig. 1. DSC analysis for pure paraffin and paraffin/graphite

The graphite matrix was made by compacting expanded graphite (EG) to the desired bulk density. EG is prepared from natural flake graphite to maximize the mass fraction of paraffin to be absorbed into its porous structure. The natural graphite sample is first converted to expandable graphite by using some chemicals. EG is then obtained by rapid expansion and exfoliation of expandable graphite in a furnace over 1000 °C for 60 s. A detailed description of the expanded graphite production method is presented comprehensively in literature [11]. In this study, expandable graphite (>%98 purity, 50 mesh, and 700ml/g) was supplied by ProGraphite GmbH (Germany) and EG was obtained. Then, EG was compacted to obtain a bulk density of 75 g/L graphite matrix in an aluminum mold using Instron Universal Testing System (Instron 3382).

A hollow cylinder of graphite matrix as supporting material for PCM was manufactured. The hollow cylinder has 10 mm thickness and 18 mm inner diameter. To produce PCM/graphite matrix composite, the graphite matrix was immersed in a liquid paraffin bath (RT42) at 70°C in a vacuum for about 4 h to achieve saturation. The PCM is impregnated to the graphite matrix through capillary forces [11,13]. It is also emphasized that the capillary forces do not allow any PCM leakage from the matrix to the outside while melting. The PCM quantity filled in the PCM/graphite matrix is 13.88 gr. The mass ratio of the paraffin in the PCM/graphite matrix composites is about 91%. The total porosity of the graphite matrix was calculated about 88 % by using impregnated PCM amount.

Fig. 2 shows the scanning electron microscope (SEM, Zeiss EVO LS10) images of the EG matrix and the PCM/graphite matrix. It is shown that compressed EG exhibits worm-like particles (Fig. 2a). As can be seen in Fig 2a, there are some non-interlocking areas between EG layers. Fig. 2b displays the morphology of the PCM/graphite matrix composite. The honeycomb-like network built by the overlapping and intersecting of graphite flakes (Fig. 2a) of the EG matrix was coated with paraffin [24]. It can be concluded that the EG layers adsorb most of the paraffin in their pores.



Fig. 2. SEM images: graphite matrix (a), pcm/graphite matrix (b)

Fig. 3 shows the optical images of PCM/graphite matrix sample before and after heating samples to 75°C. PCM/graphite matrix keeps its form without leaving any stain on the paper. This result shows that the PCM/graphite matrix is leakage-proof until 75°C.



Fig. 3. Leakage test of PCM/graphite matrix; T=30°C (a), T=85°C (b)

# 2.2. Experimental setup and procedure

The experimental setup used for battery test is given in Fig. 4. It consists of five main parts: test section (PCM/graphite matrix and Li-ion cell), electronic dc load, data logger, thermal camera, and PC.



Fig 4. Experimental setup; schematic view (a), photograph (b) The construction details of the test section (test/battery module) are shown in Fig. 4b. Test section comprises li-ion cell (1s) and PCM/graphite matrix with a height of 60 mm and outer diameter of 38 mm. A commercially available li-ion cell (Panasonic-Sanyo NCR 18650B) was used in the test module. The specifications of the battery module are summarized in Table 2.

Table 2. Li-ion cell/pack specification

Specification	Value
Form factor	1s
Capacity nominal, mAh	3250
Voltage nominal, V	3.6 V
Specific energy (Wh/kg)	243
Energy density (Wh/L)	676
Total weight of pack (gr)	48 (cell)+13,9 (PCM/graphite matrix)

To monitor the temperature response along with the li-ion cell, eight thermocouples of Ttype (Th1-h8) with an accuracy of  $\pm 0.5^{\circ}$  (supplied by omega) were placed on the li-ion cell. The thermocouple locations and li-ion cell dimensions are shown in Fig. 5. A thermal camera (Flir, A20 thermovision) was also used to visualize the thermal image of the PCM/graphite matrix outer surface. Transient temperature measurements were recorded via a data logger system (PCE-1200) by 5 s intervals. The battery was discharged of a 2.5C rate (8 Amper) using a Chroma electronic dc load (CH-63004-150-60).



Fig 5. The points of the temperature measurements on the Li-ion cell

All the experiments of natural air cooling (reference case) and PCM/graphite matrix were carried out in a conditioned room, where the ambient temperature is 25°C. Experiments were terminated by reaching the limit operating temperature (55°C) or cut-off voltage (2.5 V) value whichever comes first.

## EXPERIMENTAL RESULTS AND DISCUSSION

Effect of the PCM/graphite matrix on the thermal management of li-ion cell is tested experimentally compared to the case of natural air cooling at 2.5 C rate. The time history of temperature variations at eight evenly spaced locations and the thermal images are presented in Figures 6-7 to evaluate the thermal performance of each battery pack configuration. The voltage-discharge capacity (V-Ah) variation and energy capacity (Wh) is also given in Figure 8-9 to reveal the electrical performance of each battery pack.

Heat transfer through a porous medium of graphite matrix, which has a high ratio of heat transfer surface to volume, has been considered as heat flow along highly conductive abundant thermal paths. This advantage of the graphite matrix accelerates the process of carrying and storing heat in the phase change material. Heat transfer in such a medium occurs by conduction [13, 25]. The natural convection heat transfer is suppressed within pores smaller than 10 mm [25]. These pore sizes are confirmed by SEM images in Fig.2.

Temperature profiles of each battery pack configuration are shown in Fig.3. For the natural air cooling case, surface temperatures of the li-ion cell increase steeply with time in Fig.3a. In this case, the heat dissipated from the outer surface of li-ion cell is not transferred effectively by air cooling because of the low thermal conductivity of 0.025 W/m.K (at 25°C) and also low natural convection rates. This behaviour causes reaching the limit operating temperature (55 °C) in a shorter time of 8.5 mins. Besides, the non-uniform temperature profile along with the cell (T<sub>maximum</sub>-T<sub>minimum</sub>=T<sub>8</sub>-T<sub>1</sub>=5 °C) occurred. However, for the PCM/graphite matrix, the increment rate of the surface temperature is lower than the natural air cooling (Fig. 3b). Also, more uniform temperature gradient is observed by the PCM/graphite matrix. This is the result of the considerable increase of heat dissipation rates throughout the li-ion cell surface to the medium and the thermal energy storage capacity of PCM. The higher heat dissipation rate achieved by abundant thermal paths ensured the higher heat transfer rate. Dissipated heat in the PCM/graphite matrix is absorbed by paraffin in the form of sensible (period of temperature increasing) and latent heat (period of phase transition). Here, the PCM/graphite matrix act as a heat sink. For example, at=8.5 mins, it is seen from the fig 3a and b that recorded maximum surface temperatures are 55 °C and 37 °C for PCM/graphite matrix and natural air cooling, respectively. On the other side, the maximum surface temperature difference decreased to the value of 1°C ( $T_{maximum}$ - $T_{minimum}$ = $T_8$ - $T_1$ ) by PCM/graphite matrix. These outputs reveal that for the PCM/graphite matrix, operating temperature and temperature difference on the liion surface (T<sub>8</sub>-T<sub>1</sub>) are approximately 34 % and 80 % lower compared to natural air cooling, respectively. Therefore, the PCM/graphite matrix also provides a longer operating time in reliable operating temperature. It is shown from Figure 3b that operating time in reliable temperature ranges increases up to 11 mins with an increase of 30 % compared to natural air cooling. It should be remembered that experiments were ended with reaching the limit operating temperature (55 °C) or cut-off voltage (2.8 V) value whichever comes first. For natural air cooling and PCM/graphite matrix, operating temperature and cut-off voltage value were observed as a limit experimental condition, respectively. In addition, PCM quantity and its melting temperature are significant parameters on the thermal performance of the PCM/graphite matrix. It is shown from Fig 3b that temperature values along the li-ion cell did not exceed the melting area of RT-42 (T<sub>m</sub>=38°C-43°C). In other words, solid-liquid phase transition in the PCM/graphite matrix did not occur during the experiment. This reveals that heat is not absorbed in latent heat form in the PCM/graphite matrix. So, the high energy storage capacity of latent heat is not utilized. The only thermal energy storage mechanism is sensible heat.



Fig 6. The time history of temperature along the li-ion cell surface: natural convection case (a), the PCM/graphite matrix (b)

Temporal thermal camera images are given every 4 minutes in Fig. 7. The final thermal image corresponds to the time of reaching the limit condition (limit temperature or cut-off voltage) at which the experiment is completed. For natural air-cooling configuration, thermal images are presented in Fig 7a. It is clearly shown that temperature distribution on the li-on surface is not uniform axially. Because the heat generation rate is not the same at a different position inside a Li-ion cell. It is known that the majority of electrochemical reactions occur at the electrodes [2]. On the other side, ascending warm airflow due to the natural convection also causes a temperature gradient. Therefore, it is shown that regions closest to the positive electrode have higher temperature values. However, for the PCM/graphite matrix in Fig. 7b, temperature measurements are lower and nearly uniform. Here, it should be emphasized that thermal images in Fig 7b present temperature contours of PCM/graphite matrix outer surface. It is observed that outer (Fig. 7b) and inner (Fig. 6b) surface temperature measurements of the PCM/graphite matrix are close to each other. This behaviour evaluates the higher thermal diffusivity and higher heat transfer rates radially and axially. The temperature field on the liion cell surface for natural air cooling and PCM/graphite matrix support the thermocouple measurements given in Fig. 6.



Fig. 7. The time history of thermal camera images: natural convection, li-ion surface (a), PCM/graphite matrix (outer surface) (b)

Electrical performance findings (discharge capacity, Ah -voltage, V and power/energy capacity, Wh) for each battery pack configuration are given in Fig. 8 and 9. It is shown from the Fig. 8 that utilized capacity values are 1.2 Ah and 1.4 Ah for natural air cooling and PCM/graphite matrix, respectively. It should be expressed that the utilized capacity of cell using the PCM/graphite matrix, which is higher 17 % than natural air cooling, is achieved at reliable operating temperature/voltage range. However, the voltage decrement rate is lower for air cooling case. This can be explained by higher temperature measurements on the cell, which provides higher ionic conductivity and so better performance for air cooling. On the other side, reaching the limit surface temperature of 55 °C inhibits the longer-duration use and more capacity usage of cell. Power/energy capacity (Wh) for both case is given in Fig.9 comparatively. Power capacity means power delivered for an hour by the battery. It is illustrated from the figure that li-ion cell with PCM/graphite matrix deliver 8% more power (3.87 Wh) compared to reference case (3.59 Wh) for an hour. This behaviour evaluates that more amount work performed is obtained by the case of PCM/graphite matrix cooling under reliable operating conditions.



Fig 8. The capacity-voltage variation of li-ion during the discharge period



Fig 9. Energy capacity of li-ion cell for both thermal management strategies

# CONCLUSION

In this experimental study, the effect of PCM/graphite matrix on li-ion battery thermal management is conducted. The results reveal that the PCM/graphite matrix has remarkable potential in a passive battery thermal management system. The temperature is successfully regulated and uniformly distributed throughout the li-ion cell. For the PCM/graphite matrix, the following specific conclusions can be drawn:

- For the PCM/graphite matrix, operating temperature and temperature gradient on the li-ion surface is decreased by 34 % and 80 %, respectively.
- For the PCM/graphite matrix, the operating time within safe temperature limits is increased 30 % compared to natural air cooling.
- For the PCM/graphite matrix, the utilized capacity is increased by 16 % compared to natural air cooling.
- The leakage issue was eliminated by the capillarity effect using graphite matrix without a need for external sealing material.
- Heat transfer takes place by dominant conduction for the PCM/graphite matrix.

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# COMPARISON OF CORONA-QUENCHING AND EFFECT OF PRECIPITATED DUST LAYER IN AN ELECTROSTATIC PRECIPITATOR

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#### ABSTRACT

During the operation of electrostatic precipitators, various influencing phenomena may occur, which may decrease the equipment's operational efficiency. One of these phenomena is corona-quenching, caused by the space charge of particles transported in the flowing gases that makes it difficult to develop corona discharge. Another phenomenon is the build-up of precipitated dust layer on the collecting electrode. Dust with low and high resistivity need to be distinguished, because different issues may appear in the two cases. In special circumstances even back-corona may appear, which results in very low efficiency. Though the phenomenon is known, the underlying cause and necessary intervention is not always clear.

Laboratory measurements investigated effects of dust layer with different resistances in the first phase of the research. A street arrangement was built, the collecting electrodes being metal sheets, while the corona electrode was an electrode from an existing electrostatic precipitator. Switching on and continuously increasing high DC voltage, the current was measured from the partial discharges. During the measurements, the corona current suppression, as well as the back-corona phenomenon were also observed.

In the continuation of the studies, the laboratory measurement and the preparation of static simulations took place in parallel. We cannot measure the space charge directly, but we can infer its effect during the simulations. Three-dimensional FEM electric field simulations were performed, with the same geometric parameters as the laboratory arrangement. First, we determined the current - electric field strength, then the field strength - space charge characteristics, and finally, we deduced the current - space charge characteristic. Increased space charge drastically reduces the corona currents, in extreme cases completely suppressing them. From the reduction of the separation efficiency of electrostatic precipitator, the problem in the separation chamber can be inferred.

Our results allow the understanding the underlying phenomena of the voltage-current characteristics. Therefore the causes of poor separation efficiency can be revealed and the necessary steps towards a more effective operation can be designed.

Keywords: electrostatic precipitator, corona-quenching, dust, corona discharge, COMSOL

#### **INTRODUCTION**

Air pollution is becoming a significant problem in more and more parts of the world. Rapid economic development has led to a dramatic increase in pollutant emissions and an increasing trend in energy consumption [1]. Electrostatic precipitators (ESP) are often used, mainly in large producing countries, but can also be found in many parts of the world. The function of ESPs is to separate the different dust particles from the gases flowing through the equipment, in which the filtration is carried out utilizing electric field strength and Coulomb force.

The technology has many advantageous features, including 95-99% dust separation efficiency [2, 3]. However, achieving the target value depends on various physical parameters [4], and equipment must be reviewed frequently to ensure proper separation [5]. A typical case is a change in the separation efficiency after a change in the dust emitting technology. The topic is current due to the increasingly stringent environmental regulations, particularly the requirements for smaller and smaller dust particle sizes, whereby the concentration of the output dust must not exceed the required quantity.

The common problem is that the electrostatic precipitators produced decades ago were designed to handle pollution with larger particle sizes and cannot meet the requirements with the original operating conditions. Considering that new equipment is costly (in the million dollars range), upgrading existing equipment is a common way to improve separation efficiency [6].

As a result of developments, unexpected phenomena may occur inside the equipment that requires a deeper understanding of processes. Various phenomena, such as back-corona, corona-quenching, or effect of precipitated dust layer on electrodes, are known. However, most numerical models cannot handle these different effects simultaneously [7,8,9].

Voltage-current characteristics are used for high-voltage measurements, such as investigating corona discharge near the earth's surface when lightning develops or insulation diagnostic improvements [10] [11]. In many cases, the V-I characteristic can also be used to investigate the operation of ESPs and related phenomena.

Our research aims to solve an industrial problem; due to the change of firing technology, the dielectric properties of dust were changed in the plant. Compared to the previous operation, the level of emissions have drastically increased and the exact cause has not yet been determined. By monitoring the changed current-voltage characteristics, we try to reproduce the same result with the help of laboratory measurements.

# **TYPICAL PHENOMENA DECREASING THE EFFICIENCY OF ESPs**

#### Corrosion

Corrosion occurs during the maintenance period because during regular operation, the temperatures are higher than the dewpoint. In those cases, when the operating temperature is under boiling point and water gets into the ESP chambers, it could be a problem also. The phenomenon must also be closely monitored when operating the wet ESP [12].

The formation of corrosion processes must be considered in electrostatic precipitator; in our case rust would be highlighted. The process can have the most significant effect on the corona electrodes. Still, from the electrical point of view, it is sufficient to examine the end of the electrodes, where corona discharge appears. As the radius of curvature increases, the electrical field distortion effect causing partial discharge is smaller [13].

# **Collection of dust**

In case of inadequate rapping, the precipitated dust layer with a thicker diameter is adhering to the collecting electrodes. In that case, when collecting electrode adheres to a low resistivity ( $10^5 \Omega m$ ) dust layer, the charges will pass through the dust layer in a short period and no significant charges will accumulate on the surface. The voltage-current characteristic is regular.

The situation changes as the resistivity of the dust layer becomes higher (>10<sup>8</sup>  $\Omega$ m). The charge accumulation is considerable, but the dust layer's electric field strength is not high enough to start a back corona discharge. In such a situation, corona-current suppression can be observed. This is the case when the dust layer is relatively large in thickness [14].

At very high resistivity  $(10^{11} \Omega m)$ , on the surface of dust a very high amount of charge can accumulate, despite the thin dust layer, so that the electric field strength within reaches the value that produces back corona [15,16].

# Back corona discharge

With a high resistivity dust layer, the charges can slowly escape from the surface of the particles, so that in some places, the accumulating charges create an electric field, which creates a breakdown in the dust layer. At the points of breakdown, corona discharge appears (back-corona), the charge of which is contrary to the sign of discharge of corona electrodes [17]. It decreases the separation efficiency because, with the appearance of discharges dust explode back into the gas stream, and it can deliver a considerable amount of positive charge to the flow space that dramatically reduces the significant negative space charge [18]. Brush discharge starts from the discharge points, which can easily be transformed into a strike over the separation space. This can lead to unnecessary power supply cut-off.

# **Corona-quenching**

The dust particles flowing into the electrostatic precipitator begin to charge as they arrive in the ion cloud. The charged dust creates an electric field. The corona-quenching is caused by this phenomenon. Due to the space charge, the original electric field distribution in the separation chamber changes [19], the surface's electric field strength at the end of the corona electrodes decreases, which results in a reduction of the corona current. The sign of the dust space charge is the same as the sign of the corona electrode's voltage. Though the phenomenon is known, it is complicated to model under laboratory conditions, nor is it easy to measure accurately [20]. It is a typical case that we try to infer the value of the space charge from the current-voltage characteristics.

# LABORATORY MEASUREMENTS

# Corona discharge examination

Measurement of the voltage-current characteristics of corona discharges is a widely used practice for controlling electrostatic precipitators' operation. The V-I characteristic can be used for diagnostic purposes [21] [22], because changing the operating parameters or the appearance of a specific fault modify these curves. With the help of laboratory measurements, the effect of various errors can be predicted because by these, we already know how the V-I curves change.

Although many articles on this topic have been published, there are still special cases where the measurement of V-I curves may provide new information [23, 24]. Such

measurements are also very beneficial for checking numerical models developed for the purposes mentioned above [25].

#### **Needle-plane arrangement**

The purpose of the measurements is to investigate the discharge current from DC corona discharge. The corona discharge occurs at the tip of a needle that distorts a previously homogeneous electric field as a function of the applied voltage and the height of the needle.



Fig. 1. The applied test arrangement. Protection was built against the stress caused by the breakdown for the measuring instruments [17].

At the top of the measurement arrangement (as we can see in Figure 1.), a Rogowsky electrode can be found; in front of that, a perforated grounded plate is placed. A metal electrode is going through the hole, which is placed in the center of the grounded flat electrode. Tip radius can be changed by replacing the needle.

Because it is well known in the theory of electric fields, the needle distorts the homogeneous electric field around it, resulting in corona discharge when the intensity of the field exceeds the critical limit. With a metal needle, a resistor is connected in series so that the measured voltage drop is proportional to the corona current. The value of the resistor is 1500  $\Omega$ .

During the measurements, the DC voltage of the Rogowsky-electrode was continuously increased until the corona discharge started. The voltage values were proportional to the discharge current then recorded for each 3-5 kV DC increase. The test voltage was increased to breakthrough so that a measurement curve typical of the entire operating range of the corona discharge could be generated from the measured values. These measurements were performed for several needle heights.



Fig. 2. Corona current as a function of the applied voltage.

Figure 2. shows three different curves in function of the height of the needle for positive corona current. The exponential aspect of curves and variation of the ignition voltages as a function of needle height can be clearly seen. In these measurements, the breakthrough occurred at 60 kV for the case 1,75 cm needle and around 90 kV in the case 0,5 cm needle. If the distance of the metal plate and Rogowsky electrode increases or the radius of the needle changes, the exponential nature of the curves follow the characteristics [26].

In the next phase of research, a so-called street arrangement of an electrostatic precipitator was modelled.

#### Effect of corrosion

Due to corrosion processes, the corona electrode's spikes are less durable and more easily damaged by the impact of electric forces; therefore their curvature radius increases. In our case, it needs to be kept in mind that at short distances, the intensity of corona discharge also depends on the diameter of the radius of curvature.

Examining the effect, a piece of the electrode was subjected to intensive corrosion (soaking in water and then drying during cycles in a high humidity atmosphere). Experience has shown that the corrosion processes primarily affect the frame of the electrode, while the spikes remain almost intact. From this examination, it can be concluded that rusting can not cause unexpected operation electrically and in the short term. However, from a mechanical point of view, strong corrosion can be more critical during operation.

# Effect of precipitated dust layer

Generally, in a laboratory, the measurement of the voltage-current characteristic of an electrostatic precipitator is performed using a test arrangement comprising a portion of the high voltage corona electrodes and a grounded collecting electrode. For test voltages connected to high-voltage electrodes, record the value of the corona currents.

For the measurements, we built a new arrangement. A one-meter-long part of a high voltage electrode was used between two 1 m\*1 m earthed parallel plates. The distance between the plates was 30 cm, corona electrodes were at half distance, 15 cm from both electrodes. The collecting plates were connected to each other, so both sides of the discharge could be measured. Some inaccuracy in the arrangement is due to the fact that not all charges flow between the two electrodes, but their magnitude is negligible. The high voltage electrode was removed from an existing industrial electrostatic precipitator.

This arrangement is suitable for modelling the precipitated dust layer on the surface of the collecting electrode. Some of these measurements are shown in Figure 3. The curves of the blank model were consistent with the data we recorded during an on-site measurement. This can be considered a reference curve or an initial curve.



Fig. 13. Voltage-current characteristics of ESP model with different layer covering the collecting electrode

Empty model, or in our case, measurement without dust, was the reference curve (case 1). When a low resistivity ( $10^5 \Omega m$ ) dust layer was applied to the collecting electrode (Case 2), there was no significant change in the V-I curves from the initial value. If the resistivity of the dust layer is higher, corona current suppression can be observed (Case 4). At very high specific resistance ( $10^{11} \Omega m$ ), the dust layer can accumulate very high charges despite the thin dust layer. In case 3, the high corona current calls for consideration. In the present case, it should be known that what we are measuring is not only the current from the corona discharge, but also the charge current flowing towards the corona electrode by the positive ions passing through the dust layer. The field strength within the dust layer reaches the value that produces back corona. The harmful effect of the back-corona was explained in section 2.3.

# SIMULATION

The evolution of computer programs over the past decades allows creating simulations alongside measurements. The models and measurement results can be compared to verify the model and develop models that simulate situations that are difficult to measure in everyday life. In an industrial plant, the current can be measured, the charge accumulated by the dust can and its effect can be estimated. If the real case can be modelled, the electric field of the measured current can be deciphered. From the change of the original distribution of field, its dust charge can be estimated. Knowing this will make it easier to determine the cause of the problem, such as high dust flow. During our simulation, we used the software COMSOL.

# **Electric field distribution**

The 2D simulation arrangement is similar to the laboratory measurement. The drawn shape of the corona electrode is also identical to the real piece of the electrode. We calculated the corona electrodes with a voltage of (-65) kV during simulations while collecting electrodes had 0 V potential. In the closed range, the air in the COMSOL database was set. A rectangular cross-section region is defined with space charge between the corona and collecting electrodes,

up to 2-2 mm from the electrodes. The model does not calculate for dust particles in the medium, but it is known that the space charge is due to the charged dust.

We compared the electric field and voltage distribution during our investigations by changing the value of the space charge.



Fig. 14. Electric field and voltage distribution in ESP simulation

Maximum field strength is created at the end of corona electrodes because the end of electrodes hangs into previously homogeneous field strength, distorting electric field, thickening field lines around its surface. The maximum value was 6.23 kV/mm, where the red colour indicates its location. Approaching the corona electrode, the inhomogeneity of the high electric field strength can be very well observed. The equipotential lines around the pointed parts are dense; the simulation resulted in values between 0 and 1 kV/mm a few millimeters away from the electrode. Looking at the figure on the right, the voltage distribution is as expected. Near the corona electrodes the voltage is around 65 kV and close to the collecting electrode or on the other side, the space is near 0 V potential.

# Corona current, space charge and electric field characteristics

If the space charge range increases, maximum electric field strength begins to decrease. This is explained by the fact that the density of the equipotential lines of the electric field decreases as charges adhere to the particles of the inflowing dust. The reduction in field strength is associated with the decrease in the intensity of corona discharge and the value of corona current. Fig. 5 (b) shows simulated results with maximum field strength as a function of space charge. The next step was to determine field strength – current characteristic.

During laboratory measurements, the arrangement is the same as described in 3.4. We could tell voltage-current results. In the COMSOL model, if the original laboratory arrangement was set without space charge and we set the same voltage on the electrode, we could determine the maximum electric field strength. It can be assigned to laboratory measurements and determine the maximum electric field strength and current characteristic, as Fig. 5 (a) shows.



Fig. 15. (a) Corona current as function of maximum electric field strength and (b) electric field strength as a function of space charge

By comparing the E-I end E- $\rho$  characteristics, it can be seen that the common point is the electric field strength. If a change occurs, for example, the space charge increases, the maximum field strength decreases, which means that the corona current will also decrease. Due to the relation, the value of corona current as a function of space charge can be determined.



Fig. 6. Corona current as a function of space charge

In recent years we examined electrostatic precipitators operating at a voltage of between 55-65 kV, the two curves in Fig. 6 model these two extreme values. It can be clearly seen that at 30-40  $\mu$ C/m<sup>3</sup> space charge, corona current can drastically decrease or even stop. It should be added to the result that different variables have to be taken into account to accumulate space charge. On the one hand, the charges are fed by the partial discharge, so if the corona current ceases, the extra charges entering the separation chamber are also reduced, and an uncharged ,dust cloud' flows, dust blocks are formed. On the other hand, it provides valuable information for determining the composition of the dust at some level, knowing that smaller dust particles can accumulate more charges. The addition was necessary because such space charge cannot physically be created.

In practice, ESPs with a large corona quenching phenomenon have experienced decreased dust emissions when impulse mode was used.

#### CONCLUSION

In this article, we reproduced several factors that may affect the efficiency of separation. Based on measurement results, it can be seen that an electrostatic precipitator can be modelled under laboratory conditions, but its operational condition is challenging to be model directly. Numerical simulations are suitable for this purpose, which can be used to perform space charge calculations. FEM software was used to investigate electric fields in a real ESP geometry.

In this article, we showed two main factors, the effect of the precipitated dust layer and the effect of the corona-quenching phenomenon. Previous experience is that the voltage-current characteristics depend on the resistance of dust. Without back corona, the value of corona current is less than without dust. Still, it does not decrease to such an extent that this phenomenon is responsible for the dramatic decrease in current. With corona-quenching, the corona current decreases and can even eliminate it beyond a certain limit by increasing the value of space charge. From the characteristics in our case, we can conclude that the dust space charge has a more significant effect. Knowing the problem, we can find out the solution sooner in later research. The characteristics are in line with research in various literature.

Based on the research work, it can be stated that certain phenomena can be detected most effectively from the intensity of the change of the current-voltage characteristics. In the case of low separation efficiency ESPs, different methods can be used to reduce emissions. Often the frequency of knocking or the average supply voltage is changed, but increasing the humidity can also be a solution. We can solve unexpected situations more quickly if we know the cause of it better.

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# ENHANCED CONTROL ALGORITHM FOR SINGLE-PHASE ACTIVE RECTIFIER UNDER LOADED OPERATION

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#### ABSTRACT

Single-phase active rectifiers have wide application area in industry. Third order harmonic is generated to the grid during operation of single-phase active rectifier due to second order oscillation in DC link voltage. The third order harmonic component increases grid current THD value. In this paper, an enhanced control algorithm is proposed to prevent the second order oscillation transferred to the electric grid. Therefore, a low THD value of the grid current is ensured, which satisfies the specifications about the grid distortion. A SOGI filter is used in the proposed controller by adding feedforward in DC link controller. To show the effectiveness of the proposed controller, a simulation model of single-phase active rectifier is constructed and analysed through the conventional and the proposed techniques. The conventional method and the proposed method are investigated under different loading conditions. The performance results shows that the grid current THD values under full load operations are 2.14% and 1.23% via the conventional method and the proposed method. In addition, the THD values are 3.64% and 3.30% under 20% loading situation for the conventional and proposed techniques, respectively. As a result, the proposed method has lower THD values under various operation conditions.

**Keywords:** Active rectifier, total harmonic distortion, SOGI filter, DC voltage oscillation, second order harmonic

# **INTRODUCTION**

Rectifiers are devices used to transform AC signals into DC signals. Rectifiers are mainly divided into two groups such as uncontrolled and controlled rectifiers. The DC-link voltage is constant for uncontrolled rectifiers, and can be variable with controlled rectifiers. Besides, lower ripple ratio of output voltage can be obtained in controlled rectifiers [1, 2]. Controlled rectifiers can be either thyristor-controlled or transistor-controlled. Transistor-controlled rectifiers, also named as active (or PWM) rectifiers, are based on switching components (i.e. MOSFET and IGBT), and grouped according to phase type as single-phase and three-phase [3-5].

Single-phase active rectifier topology has many application areas from home appliances to industrial systems because of their benefits of high reliability, high efficiency and low size. Some applications of single-phase PWM rectifiers consist of small wind energy, variable frequency drive (VFD) [1, 6, 7], uninterruptible power supply (UPS), railway traction system [8], wireless power transfer [9, 10], charger of electrical vehicle (EV) [11, 12], etc. Single-phase active rectifiers are also capable of obtaining high power factor value with reduced harmonic components in current.

Single-phase active rectifier, a part of controlled rectifiers, needs a control algorithm to realize a constant output DC voltage [13, 14]. The control algorithm is generally based on current control [15] or power control [16]. In literature, several control methods exist depending on current and power control. These control methods are hysteresis control, proportional integral (PI) control, proportional resonant (PR) control, deadbeat control, sliding mode control, model predictive control, etc. [12, 17]. Linear controllers such as PI and PR are mostly preferred among the controllers although the other controllers have a good dynamic response [5, 18].

Despite having many advantages and application areas, single-phase active rectifiers have an essential drawback due to power mismatch between AC side and DC side. This power mismatch results in second-order harmonic fluctuation in DC side, namely double frequency of AC grid frequency occurs in DC link voltage [11, 19]. The second-order harmonic component in DC link voltage leads to third-order harmonic component in AC side. The current drawn from grid includes third-order harmonic that increases total harmonic distortion (THD) value of AC current and distorts the grid [2, 20].

In this study, a novel control algorithm is proposed to reduce current harmonic components in AC grid. In this way, current THD value is decreased to level that is more acceptable. In order to lessen current harmonics in grid side, a second order generalized integrator (SOGI) filter is integrated in the control algorithm. To verify the proposed controller, a single-phase active rectifier is designed and constructed in a simulation environment. The effectiveness of the proposed control method is investigated under different loading ratios. The simulation results show that the proposed control algorithm can reduce THD value and smooth grid current under different load values.

# DESIGN AND OPERATION PRINCIPLE OF SINGLE-PHASE ACTIVE RECTIFIER

Circuit configuration of grid-connected single-phase active rectifier is demonstrated in Fig. 1. The single-phase active rectifier consists of an H-bridge converter, a smoothing filter and a DC link capacitor. The DC link voltage is controlled through triggering electronic switches (S1, S2, S3 and S4) that can be MOSFETs or IGBTs according to the power rating and switching frequency. In order to diminish high switching ripple harmonics, a smoothing reactor ( $L_f$ ) is inserted between the grid and the converter. The value of the smoothing reactor is calculated by using Eq. (1) [1]. On other side, the DC link capacitance is applied to maintain low output ripple in DC voltage. The load is connected in parallel with DC link capacitor. The minimum DC link capacitance value is determined as in Eq. (2) [2]:

$$L_f = \frac{3V_g^2}{20\pi f_0 P_N},$$
(1)

$$C_{dc} = \frac{0.15P_N}{\Delta V_{dc} V_{dc} f_{sw}}.$$
(2)



Fig. 1. Circuit diagram of single-phase active rectifier

# PROPOSED CONTROL ALGORITHM

The control algorithm of active rectifier with conventional DC link controller is demonstrated in Fig. 2. The current control is performed in dq frame. Thus, the measured grid current is transformed from  $\alpha\beta$  frame into dq frame. The grid current is  $\alpha$  component. Besides, the grid current is shifted by 90° to acquire  $\beta$  component. Then the reference DC link current,

obtained from DC link controller, is added to grid current components in dq frame. The reference DC link current is added into d component. The reference q component is zero because of no reactive power compensation. The PI controller controls the error current signals in dq frame. After that, a reverse dq- $\alpha\beta$  transformation is performed to obtain reference voltage signal. Lastly, SPWM method is applied for generating pulses of switches. An oscillation in 100 Hz occurs when a load is connected to DC link capacitor. This oscillation in DC link is transferred to current controller and leads to third order harmonic in grid current, which distorts the grid current and increases its THD value.



Fig. 2. Control algorithm of active rectifier with conventional DC link controller

In this study, a SOGI filter is used in DC control algorithm to eliminate 100 Hz oscillation transferred into current controller. The SOGI filter is a type of band-pass filter. The improved DC link controller is demonstrated in Fig. 3. The DC link voltage is firstly passed through a SOGI filter. Then, the output of filtered DC voltage signal is added as feedforward in dc link control algorithm. The transfer function of SOGI filter is given in Eq. (3).



Fig. 3. Enhanced DC link controller for active rectifier

$$H(s) = \frac{Kw_{c}s}{s^{2} + Kw_{c}s + w_{c}^{2}},$$
(3)

where,  $w_c$  determines the frequency that is let passing from the filter. It is adjusted as  $w_c = 2\pi 100 \text{ rad/s}$  in this study to let 100 Hz passing through the filter. *K* is a constant and indicates the bandwidth of the filter. Fig. 4 shows the frequency response of SOGI filter for different *K* values. It is obvious from the figure that the filter bandwidth gets narrow bandwidth via lower *K* values. In this study, *K* is chosen as "1" for optimal bandwidth range.



Fig. 4. Frequency response of SOGI filter for different K values

# CASE RESULTS AND DISCUSSION

In this section performance results and discussion on results are provided. A single-phase active rectifier model is implemented in a simulation environment to examine the effectiveness of the proposed control algorithm. The parameters of the implemented model are given in Table 1.

Symbol	Meaning	Value
$V_g$	Supply Voltage	220 V
$P_N$	Nominal Power of APF	4.3 kW
f	Grid fundamental frequency	50 Hz
$f_{sw}$	Modulation frequency	5 kHz
$V_{dc}$	DC link voltage	380 V
$L_{f}$	Filter inductance	10 mH
$C_{dc}$	DC link capacitance	5 mF

Table 3. System parameters used in modelled system

Fig. 5 shows the DC link voltage under various loading percentages. The active rectifer is loaded between 20%-100% by a 20% increase each time unit. In time 0-1s, no load is applied and the DC link is charged to its reference value. The active rectifier is loaded by 20% when the time is at 1s. And then, the system loading is raised by 20% every one second. It can be seen from the figure that the oscillation in DC link increases with higher loading conditions. Besides, the grid voltage and current under different loading conditions are demonstrated in Fig. 6.



Fig. 5. DC link voltage under different loading percentages

Fig. 7 illustrates the waveforms of the grid voltage and current under full load operation. In addition, THD of current under full load is shown in Fig. 8. It can be seen that THD value is 1.23 % when the active rectifier operates under rated load value. Moreover, Table 2 demonstrates a comparison of current THD values of the conventional control and the proposed control method for five different loading situations. The load in DC side is changed from 20% to 100% to perform the comparison. It is obvious that the proposed technique shows better performance than the conventional method for all loading conditions. The current THD values are lower when the proposed method is applied even 20 % loading condition. The performance superiority of the proposed method is clearer under higher loading conditions. The THD of the grid current is 1.23 % with the proposed technique while it is 2.14 % when the traditional method is used.



Fig. 6. The grid voltage and current under different loading conditions.



Fig. 7. The grid voltage and current under full load operation



Fig. 8. THD value of the grid current under full load operation by applying the proposed method Table 4. Comparison of grid current THD values

Loading/Current THD	Conventional Control	Proposed Control
20 %	3.64 %	3.30 %
40 %	2.46 %	1.89 %
60 %	2.22 %	1.42 %
80 %	2.16 %	1.30 %
100 %	2.14 %	1.23 %

The proposed method is analysed through loading the active rectifier from 20% to 100%. In addition, a comparison is performed with the conventional controller. The proposed method has lower THD values under various loading conditions. The THD values are 3.64%, 2.46%, 2.22%, 2.16% and 2.14% with the conventional technique under 20%, 40%, 60%, 80% and 100% loading, respectively. On the other side, the THD values are 3.30%, 1.89%, 1.42%, 1.30% and 1.23% with the proposed method under 20%, 40%, 60%, 80% and 100% loading,

respectively. It is obvious, the proposed method has better THD performance when the loading increases from 20% to 100%.

# CONCLUSION

In single-phase active rectifiers, second order harmonic oscillation occurs in DC link voltage when the load is connected to output. This harmonic oscillation is transferred to the grid side current as the third harmonic current component. The conventional controller of the active rectifier is insufficient to prevent this harmonic oscillation transfer. By the way, the third harmonic component distorts the grid current, resulting in a high THD value of the grid current.

In this study, an enhanced control method is proposed in single-phase active rectifier to mitigate the harmonic oscillation in grid current. A SOGI filter is exploited in control algorithm through adding as feedforward in DC link controller. The design and characteristic of the SOGI filter are provided. The proposed controller is investigated by implementing a single-phase active rectifier in Simulink environment. The implemented active rectifier system is analysed and discussed by applying the conventional and proposed controller under different loading percentage. The proposed control method reduces the second harmonic components once compared with the conventional method. Besides, the THD value of the grid current is diminished from 2.14% to 1.23% through using the enhanced method.

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# CONFERENCE PAPERS

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# I.4. Smart energy systems

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SYSTEM: CURRENT STATE-OF-THE-ART REVIEW AND EXPANSION
M. Sarmad, N. Tutkun. <u>LOW COST AND RELIABLE HOME ENERGY MANAGEMENT</u> SYSTEM USING GENERALIZED REDUCED GRADIENT NONLINEAR SOLVER
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D. Stanelytė. OPTIMAL DEMAND SIDE MANAGEMENT MODEL BASED ON THE INTERNET OF THINGS
A. Atay, M. M. Savrun. <u>NOVEL PARTIALLY INSULATED MULTIPORT DC-DC</u> <u>CONVERTER WITH PARALLEL OPERATION TECHNIQUE</u>

# DATA TRANSMISSION IN REMOTE POWER QUALITY MONITORING SYSTEM: CURRENT STATE-OF-THE-ART REVIEW AND EXPANSION

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# **EXTENDED ABSTRACT**

Development of Smart Grids is inevitable without various monitoring systems. One of them is Power Quality monitoring system – the newly emerging field which has been attracting more and more attention since last few years. Therefore, there are only few scientific studies related to the scope of this paper – Power Quality monitoring and its communications. It has been concluded that the absence of specific information in reviewed documents about communications for Power Quality system and the absence of massive remote Power Quality monitoring systems indicates insufficient experience in the world, including developed regions.

In general case, remote monitoring system consists of three main structural parts: measurement block, data processing and communications. The paper focuses on the third part – data transmission block: required data rate (bandwidth) reduction issues, data packet structure, some Quality-of-Service aspects and suitable communication technologies, system performance evaluation in MATLAB/Simulink. To reduce data rate, feature extraction techniques are discussed. Problem of monitoring system measurement data loss during measurement campaign is demonstrated. In addition, wireless communication network designing principles are demonstrated using "EDX SignalPro" demo version on available geographical district. It has been found that results are unique and not described neither in literature and reports, nor in legal documents and standards related to Power Quality and its monitoring (EN 50160:2010, EN 61000-4-30:2015 and IEEE Std 1159-2019).

**Keywords**: Smart Grid, Power Quality, remote monitoring, data transmission, Quality-of-Service, bit error rate

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# LOW COST AND RELIABLE HOME ENERGY MANAGEMENT SYSTEM USING GENERALIZED REDUCED GRADIENT NONLINEAR SOLVER METHOD

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#### ABSTRACT

Electricity bills are a big cost for residential owners. With system efficiency improvement the cost of electricity bills can be reduced and it can bring significant benefits to house owners. Energy management systems play an important role in system operation and control. Electricity utilities base their charges on different factors but important are demand and consumption. If the irregularities during consumption are controlled, then it can play an important role in power generation. Demand side management is responsible for lower energy demand which in turn avoids the cost of utilities, building new generators and saving the environment from pollution as well. There are some DSM techniques to optimize this consumption for both commercial and domestic users. In this paper, the process used to solve this problem is Generalized Reduced Gradient Nonlinear solver method. The load factor is basically the ratio between average load and peak load. In domestic residential, load factor remains very low due to unscheduled load consuming the power more during the peak hours. This system contains the load profile of a residential building under consideration. Proposed design will help improve the energy consumption by reducing the usage of shift-able loads during peak hours and transfer in different hours to reduce the load factor. The designed system is optimized using Excel solver, which is responsible to perform Generalized Reduced Gradient Nonlinear solver method. After applying the optimization technique, the simulation result shows the significant improvement in load curve, which can provide benefits for both generating sectors and consumers.

Keywords: Energy management, Demand side management, Load factor, Power scheduling, Excel solver.

# INTRODUCTION

A well-managed energy management system was introduced by Faisal Baig in (2013) [1]. He proposed a two-part method. One is the power management centre (EMC) which contains a graphical interface. EMC displays operating time data and maintains user log data and equipment control. The second part of this approach is to edit uploads using a single knapsack problem.

Shareef at el in 2018 at IEEE have proposed a system that often creates fair use schedules by looking at a number of factors, such as energy costs, environmental concerns, upload profiles, and consumer comfort. With the introduction of smart meters, performing control using Energy management systems with Demand response enabled machines has become possible [2]. A research paper developed by Mahapatra & Nayyar last year proposed a new way to improve the construction of homes by incorporating the concept of green construction to reduce the use of energy by a resident in their home. Their research has shown that the effect of various programs

on large-scale reductions through the Optimization based residential energy management (OREM) process shows a decrease in energy consumption showing a 35% reduction in total electricity debt [3]. The short-term opportunity to implement an energy management system is not limited to individual consumers. However, with the integration of several consumers there is great potential. Manufacturers of Smart home energy management system need to communicate in order to integrate and ensure smooth interaction at home [4]. Home energy management systems optimize energy consumption by automating the connection between load and energy source [5][6]. Through graphical response, one can realize the energy consumption. Smart home requires energy management system to optimally utilize the energy [7]. Several methods are used now a day for energy management including demand-side management (DSM), load scheduling, and many more [8].

# **PROPOSED METHODOLOGY**

In the proposed method, of whom the flow chart is given in fig1, the first stage is to figure out the nature of the load if it is shift able/non-shift able. The non-shift able load cannot be scheduled. It will remain the same. Shift able loads are further categorized in fully and partially shift able. According to the given data, a whole load schedule as given will be labelled in Excel. After that optimization tool will be applied to that objective which is to maximize the load factor. In this research, the Generalized Reduced Gradient Nonlinear Solver method is applied to maximize the load factor. It is a constrained Nonlinear Programming method. A generalized reduced gradient algorithm is proposed exploiting the staircase structure of the Jacobian matrix of the dynamic equations by using some priority principles on the partition of the variables into basic and independent sets for each time period when a reinversion is needed, and for choosing a substitute basic variable when change-of-basis occur for regularity reasons. After finding the best schedule for shift able loads it will replace the binary on/off section and set a new schedule which will improve the load factor which will be demonstrated by the load curve representation. The program terminates if the objective function is improved. Demand side management includes improvement of load curves and load factor [9]. DSM can be implemented in two ways either direct or indirect load control. In direct control the utility can save energy by switching off the load of specific consumers. While in in-direct control the utility applies some techniques like load time scheduling, thermal storage method and many more [10].



Fig 1: Flowchart of Proposed System

# LOAD FACTOR & LOAD CURVE

The load factor is one of the most important factor in Energy systems. Basically, it is the ratio of the sum of maximum load/demand of the system to the total connected load on the system. Its value remains less than 1. This factor in the power system explains how much energy is being used during a specific period versus how much would have been used during that time interval. A system is considering well consumed if its value is very close to 1. It can be improved by improving the distribution of load during the different time intervals.

Load Factor = Average Load X 24 Hours / Peak Load X 24 Hours. 
$$(1)$$

Load curve/load profile provides information of demand at a specific interval. This graphical representation of load provides a lot of useful information regarding consumption and generation need for the specified interval. This provides great help in scheduling the load consumption more efficiently. It is an important factor in deciding to generate the capacity of the system. It estimates generating cost and help out in deciding operation schedules of power station. Maximum power is the power indicated at the top of the curve. A load curve of 24 hours from midnight to noon is shown in Fig 2.



Fig 2: Load Curve of a Household for 24 Hours

# **OBJECTIVE FUNCTION**

For all possible DSM techniques used for optimal schedule finding problem either to maximize the load factor or to reduce the cost of utility. In this problem, load factor improvement will be done by some non-linear problem solving technique using Excel solver. The objective function for load factor which has to be improved is as follows.

$$LF_{max} = \left[ \left[ \sum_{i=1}^{N} \sum_{j=1}^{J} \mathsf{P}_{(i,j)} \, \mathsf{t}_{(j)} \right] / \sum_{j=1}^{J} t_{(j)} \right] / \sum_{i=1}^{N} \mathsf{P}_{(i,k)} \tag{2}$$

for  $LF_{max}$  – the maximum load factor value,  $P_{(i,j,)}$  – power demand of the load type i at the time interval j, for i = 1,..., N, and j = 1,..., J, N – the total number of load types, J – the total number of time intervals,  $P_{tot j()}$  – the total demand power for all types of loads, where j denotes time interval number, k – time interval of the maximum demand of all load types i = 1,..., N, over all intervals j = 1,..., J.

# LOAD SHIFTING TECHNIQUE

Objective function can be optimized either by equality or inequality constraints. Load shifting technique just shift the peak load without changing the total power consumption.

Equality constraints

 $p_{new(i,j)} = p_{value} \qquad \text{for t range } \{t_k, t_h\}$ (3)

Inequality constraints

 $p_{new(i,j)} \ge p_{old(i,j)}$  for trange{ $t_0$ ,  $t_k$ } and { $t_h$ ,  $T_{tot}$ } (4)

$$p_{new(i,j)} \le p_{value} \qquad \text{for t range } \{t_0, t_k\} \text{ and } \{t_h, T_{tot}\}$$
(5)



Fig 3: Load shifting Parameters

Appliance	<b>Operation range (h)</b>	<b>Operation time (min)</b>	Average power (kW)
Fully Time Shift able			
Dishwasher	1-24	120	1.80
Washing machine	1-24	120	0.80
Clothes dryer	1-24	60	2.50
Partly Time Shift able			
Iron	16-22	60	1.00
Vacuum cleaner	9-13	120	0.50
Oven	15-20	120	2.00
Hair dryer	6-10	60	2.10
Toaster	6-10	60	1.20
Electric kettle	6-10	60	2.10
TV	6-24	660 (11hr)	0.10
Air conditioner	8-24	600 (10hr)	1
Non-Time Shift able			
Fridge	1-24	1440 (24hr)	0.15
Indoor lighting	7-8, 19-24	480 (8hr)	0.20
Outdoor lighting	1-7, 19-24	780 (13hr)	0.10

Table 5: Load profile of household

# **RESULTS AND DISCUSSION:**

Table 1 include a household load profile which includes all common appliances that are being used in every home. Some of the appliance have to operate in specific hours or use 24 hours. These appliances are non-shift able appliances. Some of the have no specific time to operate these are shift able and partially shift able appliances. Using optimizing technique, the load factor which represent the behaviour of system that how well system is consuming energy and

how much is being wasted in loses. Results achieved with the help of Generalized reduced gradient nonlinear solver method are discussed in this section.

The schedule of Fully shift able loads and load curve values before applying optimization technique give down in Table 2.

Sr. No	Time (Hrs)	Base	Dish washer	Washing Machine	Clothes Dryer	Time (Hrs)	Base Load	Old Load Curve
		Loau						(watts)
1	1	250	1	1	1	1	250	5350
2	2	250	1	1	0	2	250	2850
3	3	250	0	0	0	3	250	250
4	4	250	0	0	0	4	250	250
5	5	250	0	0	0	5	250	250
6	6	250	0	0	0	6	250	5750
7	7	250	0	0	0	7	250	350
8	8	250	0	0	0	8	250	1350
9	9	250	0	0	0	9	250	1850
10	10	250	0	0	0	10	250	1850
11	11	250	0	0	0	11	250	1350
12	12	250	0	0	0	12	250	1350
13	13	250	0	0	0	13	250	1350
14	14	250	0	0	0	14	250	1350
15	15	250	0	0	0	15	250	3350
16	16	250	0	0	0	16	250	4350
17	17	250	0	0	0	17	250	1250
18	18	350	0	0	0	18	350	350
19	19	450	0	0	0	19	450	450
20	20	500	0	0	0	20	500	500
21	21	450	0	0	0	21	450	450
22	22	350	0	0	0	22	350	350
23	23	250	0	0	0	23	250	250
24	24	250	0	0	0	24	250	250
Capacity			1800	800	2500			
Runtime			120	120	60			

Table 6: Schedule of Fully shift able loads before applying optimization technique & system load curve

The Table 3 shows the same details but for Partially shift able loads. The highlighted blocks are the time frame in which these loads can only be scheduled. Capacity shows how much power consumption is done by that appliance and runtime shows how many minutes the devices have to operate.

Time (Hrs)	Base Load	Iron	Vacuum Cleaner	Oven	Hair Dryer	Toaster	Electric Kettle	TV	Air Conditioner
1	250	0	0	0	0	0	0	0	0
2	250	0	0	0	0	0	0	0	0
3	250	0	0	0	0	0	0	0	0
4	250	0	0	0	0	0	0	0	0
5	250	0	0	0	0	0	0	0	0
6	250	0	0	0	1	1	1	1	0
7	250	0	0	0	0	0	0	1	0
8	250	0	0	0	0	0	0	1	1
9	250	0	1	0	0	0	0	1	1
10	250	0	1	0	0	0	0	1	1
11	250	0	0	0	0	0	0	1	1
12	250	0	0	0	0	0	0	1	1
13	250	0	0	0	0	0	0	1	1
14	250	0	0	0	0	0	0	1	1
15	250	0	0	1	0	0	0	1	1
16	250	1	0	1	0	0	0	1	1
17	250	0	0	0	0	0	0	0	1
18	350	0	0	0	0	0	0	0	0
19	450	0	0	0	0	0	0	0	0
20	500	0	0	0	0	0	0	0	0
21	450	0	0	0	0	0	0	0	0
22	350	0	0	0	0	0	0	0	0
23	250	0	0	0	0	0	0	0	0
24	250	0	0	0	0	0	0	0	0
		1000	500	2000	2100	1200	2100	100	1000
		60	120	120	60	60	60	660	600

Table 7: Schedule of Partially shift able loads before applying optimization technique

Table 4 contains all important parameters which are involved in this problem. Most important of the load factor which is our objective to be optimized is shown in that particular scenario. The value of load factor is 0.2684. Maximum demand for the household is 5750 watts and minimum is 250 watts both are highlighted to look prominent. Average load demand is also calculated which is 1543.75 watts. All these parameters are calculated before applying optimization to the system.

Figure 5 shows the load curve of the system. In which complete variation of load consumption is shown graphically. As per looking at the graph that its maximum goes 5750 watts and minimum up to 250 watts. It is quite clear from this representation that variation between maximum load consumption and minimum load consumption is very large. It shows that the power consumption in this system needs improvement. For that optimization technique would be used. In this case we use Generalized Reduced Gradient Non-linear Solver. It is performed using excel solver.

#### Table 8: System Parameters before optimization

Load Factor	0.26
Max demand	5750
Average demand	1543.75
Units	37050

# The results of load curve are given below. Showing Load at y-axis and hours along x-axis.

8000

6000

4000

2000









So, all information parameters and details are obtained for that load profile of household. Now we applied our proposed optimization technique. This process is being carried out in Excel solver. Excel solver has some special built in solving methods and this optimization is being done through this tool as well. Information about that and also constraints section and more related to this task is shown in figure down fig 6.

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Select Simpl probl	t the GRG Nor ex engine for ems that are r	nlinear engine for linear Solver Prot non-smooth.	Solver Problems the plems, and select the	at are smooth no e Evolutionary er	onlinear. ngine fo	Select the LP Solver

Fig 6: Excel Solver Parameter Set for Optimization

Optimal output received for the problem will be mention now step by step. We can compare both before and after results of the problem down below. So firstly, as we had constructed a table of schedule of all fully schedulable loads. In the table 5 the same parameters after applying optimization technique are shown.

Time (Hrs)	Base Load	Iron	Vacuum Cleaner	Oven	Hair Dryer	Toaster	Electric Kettle	TV	Air Conditioner
1	250	0	0	0	0	0	0	0	0
2	250	0	0	0	0	0	0	0	0
3	250	0	0	0	0	0	0	0	0
4	250	0	0	0	0	0	0	0	0
5	250	0	0	0	0	0	0	0	0
6	250	0	0	0	0	0	1	1	0
7	250	0	0	0	0	0	0	1	0
8	250	0	0	0	0	0	0	1	1
9	250	0	1	0	0	1	0	0	0
10	250	0	0	0	1	0	0	1	0
11	250	0	0	0	0	0	0	0	1
12	250	0	0	0	0	0	0	0	1
13	250	0	1	0	0	0	0	0	1
14	250	0	0	0	0	0	0	1	0
15	250	0	0	0	0	0	0	0	0
16	250	0	0	0	0	0	0	1	1
17	250	0	0	0	0	0	0	1	1
18	350	0	0	0	0	0	0	0	1
19	450	0	0	1	0	0	0	1	0
20	500	0	0	1	0	0	0	1	0
21	450	1	0	0	0	0	0	1	1
22	350	0	0	0	0	0	0	0	0
23	250	0	0	0	0	0	0	0	1
24	250	0	0	0	0	0	0	1	1
		1000	500	2000	2100	1200	2100	100	1000
		60	120	120	60	60	60	660	600

Table 9: Schedule of Partially shift able loads after applying optimization technique

Maximum demand for the household was 5750 watts and minimum was 250 watts when we calculated according to first schedule which was before optimization but as we apply optimization the schedule changed and because of these values also change. Now maximum demand for the household is 2850 watts and minimum remain 250 watts both are highlighted to look prominent. Now as we can analyse both the variation of load demand decrease prominently which is an evidence that our rescheduling help system to improve energy consumption remain whole constraints unchanged. Important parameters such as maximum demand, average demand and unit consume are given in Table 6. Most important thing to be noticed by doing all this how much it effects the Power factor which was our main aim as well as our objective to be maximized. Load factor improvement can be seen in the table 5 Recently the load factor was low due to irregular usage of power. Its value was 0.2684 before applying optimization, but after optimization the value of load factor is improved to 0.5416. Improvement is almost 50% after applying optimization which provide us better scheduling of load to be consumed in a day.

Sr. No	Time (Hrs)	Base Load	Dish washer	Washing Machine	Clothes Dryer	New Load Curve (watts)
1	1	250	1	0	0	2050
2	2	250	1	1	0	2850
3	3	250	0	0	0	250
4	4	250	0	0	0	250
5	5	250	0	0	0	250
6	6	250	0	0	0	2450
7	7	250	0	0	0	350
8	8	250	0	0	0	1350
9	9	250	0	0	0	1950
10	10	250	0	0	0	2450
11	11	250	0	0	0	1250
12	12	250	0	0	0	1250
13	13	250	0	0	0	1750
14	14	250	0	0	0	350
15	15	250	0	0	0	250
16	16	250	0	0	0	1350
17	17	250	0	0	0	1350
18	18	350	0	0	0	1350
19	19	450	0	0	0	2550
20	20	500	0	0	0	2600
21	21	450	0	0	0	2450
22	22	350	0	0	1	2850
23	23	250	0	0	0	1250
24	24	250	0	1	0	2150
Capacity			1800	800	2500	
Runtime			120	120	60	

Table 10: Schedule of Fully shift able loads after applying optimization technique & New load curve of system





Fig 7: Load/Demand Response after OptimizationFig 8: Load Curve after OptimizationThe results of load curve are given above. Showing Load at y-axis and hours along x-axis.



# Table 11: System Parameters after optimization



Fig 9: Load Curves Before And After Applying Optimization

The results of load curve are given below. Showing Load at y-axis and hours along x-axis. As mention before an optimization applied to the system improves the improvement of load consumption. It can be graphically represented with load curve. As we can analyse from figure that the variation between maximum and minimum load is reduced which in result improves the load factor as well. Blue waveform shows the load curve before applying optimization and orange waveform shows load curve after optimization.

# **CONCLUSION:**

The proposed system is completely capable of optimizing and scheduling of load usage in a household. It's very important to optimize the usage to save energy from the utility as well as a consumer point of view. In third world countries like Pakistan and Bangladesh energy crisis is big issue and a lot of researches are under work to improve that as much as possible. In this research a very important factor of energy system known as Load Factor. It's the ratio between average to peak load at any instance. Due to bad infrastructures and un even distribution is some major cause that the load factor remains very low. Its value shows the condition of system that how optimal it is and how well it is consumed. According to most researches it values remain 25% to 30% in common household system but in this research it was also elaborated the same percentage of 25% can be seen before optimization. But after applying optimization technique load factor is improving and goes to 56% which can be seen in results section. A lot of complex systems have been proposed to obtain this objective. But using an Excel solver makes the system simpler and easier to change for different load profiles. That can be improved if we use the energy smartly proposed method is built to help out in this regard.

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# PREDICTIVE MODEL FOR STOCHASTIC LOAD OF ELECTRIC VEHICLES

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#### ABSTRACT

Nowadays due to the price increase for oil and gasoline as well as air pollution in large cities caused by internal combustion engine vehicles, more often electric vehicles (EVs) are considered as the main means of transportation. For distribution networks EVs are the source of extra load, stochastic since it depends on the movement of transport. Such an amount of extra load can overload the network and lead to faults and shutdowns as well as lead to the unacceptable drop of voltage levels. So, it is crucial to predict the amount of load and voltage drop for every node of the distribution network. Because of the stochastic nature of the load, a probabilistic method was used, in this case a Monte Carlo simulation. However, to use a Monte Carlo method an accurate model of EVs movement is required. As for now, many studies use the normal distribution to model EV movement. However, it was proven to be not quite accurate in comparison to the real-life data. In this paper, a model based on bootstrapping using real-life data is compared to the more conventional normal distribution-based models. This model is then used for Monte Carlo simulation in one of the districts in St. Petersburg. Using daily load profiles for a feeder in this district, consumers' voltage levels were found and evaluated. The probability of overload for 10\0.4 kV substations was found.

Keywords: electric vehicle, distribution network, stochastic load, Monte Carlo method

#### **INTRODUCTION**

Nowadays there is a worldwide trend towards cleaner means of transportation, in particular the shift from internal combustion engine vehicles (ICE vehicles) to electric vehicles (EVs). As of the beginning of this year, there are about 6 million EVs worldwide. The number of EVs is growing exponentially. The statistic of EVs sales shows this trend: there were 845 thousand EVs worldwide in 2014, 1.4 million in 2015, 2.1 million in 2016, 3.4 million in 2017 and 5.6 million in 2018 [1]. The same trend can be seen in Russia - over the past year and a half the number of EVs has increased by 2.71, and by 2025 it is expected to increase the number of EVs in the country up to 200000 [2].

Despite the fact that the full production cycle of EVs in terms of environmental safety is not much better than that of conventional cars, the benefits of EVs will be quite significant in large cities, where the main source of air pollution is ICE vehicles.

In terms of power grid managing, EVs are an additional load for the grid and also stochastic, which makes it more difficult to assess its impact on the power grid, as well as reduces the reliability of the power grid. For example, random behaviour when charging EVs can lead to a new load peak when EVs are added to the grid during peak load periods, which will increase the load on the power system and can lead to malfunctioning of the distribution network [3].

As a new type of load, EVs are fundamentally different from any traditional load. In particular, the moment of connection to the grid is a random value, the load from charging is large, the place of connection is also random, etc. Such a type of load is called stochastic. The traditional method of predicting the load is not applicable to predict the changes in load from EVs during the day in any area. So, to ensure safe and cost-efficient operation of the grid it became necessary to apply special probabilistic methods which study the daily load profiles from EV charging [4].

# STOCHASTIC LOAD MODELING METHODS

# **Monte Carlo method**

In this paper, the Monte Carlo method has been chosen as a probabilistic method to estimate the impact of EVs on the power grid. The Monte Carlo method is a numerical method of studying random processes based on repeated random sampling that allows calculating the probabilistic characteristics of the problem. The method is based on the law of large numbers. The method is used for complex processes that cannot be described analytically, for example, for integration of complex functions.

Input data for the Monte Carlo method are the model of the system under study, in our case, it is the model of EVs' movement and their connection to the power grid. After such a model is developed, the Monte Carlo experiments can be performed. Multiple iterations are performed using the created model of the movement of EVs, with randomly generated numbers used as the initial data for each iteration.

When a great number of iterations are completed, we get the necessary output data, which, after some evaluation, allows us to determine the probability of the event.

The Monte Carlo method was chosen for the analysis of the impact of EVs on the power grid since EVs, as randomly moving objects, are a stochastic load, the analytical evaluation of which is difficult and, in the case of complex systems, even impossible.

#### Determining the minimum required number of Monte Carlo iterations

The precision of Monte Carlo method calculations depends on the number of iterations performed. To increase precision by 10 it is necessary to increase the number of iterations by 100 [5]. However, it is necessary to take into account the fact that as the number of iterations increases, the calculation time increases and a better computer performance is necessary. Therefore, it becomes crucial to determine the minimum number of iterations, which will be enough to obtain the required level of precision [6].

To calculate the critical value of iterations for our model we must find a sufficient number of iterations for the selected confidence level and precision, in our case 95% and 0.05 respectively. For that we use the Central Limit Theorem.

The result of the Central Limit Theorem is the distribution function  $F_n(x)$  of a random variable. Let the average of the sample be:

$$\overline{X} = \frac{\sum_{i=1}^{n} X_i}{n}.$$
(1)

Then the expression for distribution function can be written as:

$$Z_n = \frac{X - \mu}{\sigma} \cdot \sqrt{n}, \qquad (2)$$

which can be described as a close to normal distribution function.

The Central Limit Theorem can be applied to any distribution. According to the theorem, the expected value of a sample is distributed normally despite the fact that the sampled data may not be. It is important to note that this is only accurate for a large value of n since the larger n is, the closer the distribution function to normal distribution.

The confidence interval can be calculated as follows:

$$CI = \left(\bar{x} - z \cdot \frac{s}{\sqrt{n}}, \bar{x} + z \cdot \frac{s}{\sqrt{n}}\right),\tag{3}$$

here x is the average sample, z is the value used to determine a confidence interval, s is the sample standard deviation, n is the number of samples. For 95% confidence interval, the value of z approximately equals 1.96.

After performing several mathematical operations this equation can be rewritten to z in terms of precision  $\phi$ . Then we can obtain the following equation in a probabilistic form:

$$P\left(-\frac{\phi}{\sqrt{n}}\cdot s < \frac{\overline{x}-\mu}{\sqrt{n}}\cdot s < \frac{\phi}{\sqrt{n}}\cdot s\right) = CL, \qquad (4)$$

where s is the standard deviation of the sample, n is the number of samples,  $\bar{x}$  is the average sample,  $\mu$  is the expected value of the population,  $\phi$  is the precision level, CL is the confidence level.

According to the Central limit theorem, the middle element of inequality (4) is distributed normally with the expected value 0 and standard deviation 1, or N(0, 1). At the same time, the distribution of the sample expected value is scaled by the factor of  $\frac{\sqrt{n}}{s}$ , so the distribution becomes standard normal. If we choose the 95% confidence level, then the upper and lower limits of the last inequality are -1.96 and 1.96, respectively.

Now to find the number of iterations it is reduced to solving the upper and lower limits of equation (4) for the only unknown n which is the number of iterations. At first, it looks like there are two unknowns: n and s. However, s is a sample deviation that can be found if we run the simulation for a small number of iterations.

Now we can calculate the number of iterations for our case. After running the simulation for 500 iterations, we get the standard deviation *s*=7.585. After that we choose the 95% confidence level and the corresponding value *z*=1.96. The solution of the equation  $\frac{0.05}{7,585/\sqrt{n}} = 1.96$  gives the result *n*=62279. Thus, to achieve the selected precision level, the

number of iterations should be about 62279.

# Comparison of stochastic load simulation using a normal distribution with using real data based distribution

In many works (e.g. [7], [8]) describing the stochastic load of EVs on the distribution grid, normal distribution is used for modelling as the most common distribution in nature. However, real data from the observations of EVs show that this stochastic load cannot be described with normal distribution. To prove it, real data obtained in the course of the study called "My Electric Avenue" conducted in England were used [9]. This study was conducted from January 2013 to December 2015. Observations were made of volunteers from different parts of England, then the anonymous results of these observations were made publicly available for further processing.

The obtained data include the date and time each EV approached the charging station, the date and time of disconnection, the battery level at the start and end of each charge, as well as travel information, namely the date and time of the start of the journey, the date and time of the end of the journey, the distance travelled and energy used during th journey.

Due to the fact that there were different numbers of volunteers participating at different times during the study, it was decided to choose a period from January 2015 to December 2015 for ease of processing and to reduce the error, since during the last year the number of participants was the highest. The higher and more even throughout the months number of participants gives a more accurate result.

To check if this data can be described with a normal distribution, of all observed EVs the ones that were charging during evening peak load were selected. After that, the number of EVs connected to the grid during peak load was obtained for each day for 11 months (since in the last 11 months the number of participants was the highest and most even throughout the months).



Fig. 1. Number of EVs connected to the grid during evening peak load
Based on the results of the data processing, a probabilistic distribution of the number of connected EVs during peak load was constructed in the form of a histogram.



Fig. 2. Probabilistic distribution of the number of EVs connected to the grid during evening peak load

Though it has a bell-like shape, which corresponds to the normal distribution, it also has two distinct peaks, indicating a possible deviation from the normal distribution. However a single graphical method is not sufficient to determine exactly if it is a normal distribution or not, so several normality tests were carried out.

For a more precise visual check, a quantile-quantile plot (Q-Q plot) was used. The Q-Q plot shows the connection between sampled data and theoretical quantiles. The proximity of sampled data to the theoretical distribution corresponds to the proximity Q-Q plot points to a 45-degree line. Normal distribution was chosen as theoretical distribution, and the number of EVs connected to the grid at load peak was taken as sampled data. The grey colour indicates a 95% confidence level.



Fig. 3. Q-Q plot of the number of EV connected to the grid during peak load distribution

The plot shows that the distribution that was checked is not normal, as the points indicating the observations are quite far away from the 45-degree line, especially in areas of large and small number of EVs. However, the graphical methods, despite their illustrativeness, are not accurate enough. For a more accurate determination of normality the Shapiro-Wilk test was used [10].

The Shapiro-Wilk test is used to test the null hypothesis: "the data are normally distributed". To prove the null hypothesis right or wrong the probability value (or p-value, p) is used. It is then compared to the level of significance, which for our case was chosen to be 0.05. If the p-value is equal to or less than the level of significance then the null hypothesis is proved wrong. Testing the sampled data's distribution for normality the value of  $p=8.763 \cdot 10^{-5}$  has been received. It is much less than the established level of significance, so the null hypothesis is proved wrong thus the sampled data are not normally distributed.

Based on these results, it was determined that stochastic load from EVs modelling using normal distribution is inaccurate and can lead to significant error. Therefore, another method of load modeling must be used.

For the load from EVs during the evening peak load simulation, the bootstrap method was used [11], which is a modification of the Monte Carlo method. This method is used when the sample size is too small to certainly conclude anything from it, or, as in our case, when the analytical determination of probability distribution is too complicated. The gist of the bootstrap method is to extract data at random from an existing sample and use it as a new "artificial" population. In our case, we randomly select from real observations a random day and then take the number of EVs that were charging during the evening peak load. Using that number additional load is found, which is added to the existing load in the distribution grid. The new scheme with renewed values for loads in the nodes is studied using the RatrWin software package.

# MODEL APPLICATION FOR A FEEDER IN ONE OF SAINT-PETERSBURG'S DISTRICTS

#### State of Saint-Petersburg's distribution grid

Currently, due to the type and location of equipment in the cable grid of St. Petersburg city, some areas may already experience a voltage drop at the consumer end during increasing load. In such areas, old equipment is installed and up to 10 transformer substations (TS) may be powered from a single cable line. In this case, the distance from the distribution substation to the first TS can be up to 4 km, and the distance between the two TSs can be 1.5-2 km. It should also be taken into account that cables in these areas have not been reconstructed for a long time, so these cables have a smaller cross-section compared to new areas of the city. The most common power cable used for the head section is a 240 mm<sup>2</sup> three core paper insulated power cable with lead sheath, and for sections between TSs are a 120 mm<sup>2</sup> three core paper insulated power cable with lead sheath. Thus, the whole chain has a length of 8-9 km, and on a single power cable there might be up to 15 transformers with a capacity from 630 to 1250 kVA.

Due to such grid configuration, sometimes the voltage can drop to unacceptable values. When this happens, the regulating capabilities of transformers, such as on-load tap-changers on the high voltage side (110/10 kV transformers) and in the rare case of no-load tap-changers on the low voltage side (10/0.4 kV transformers) are used.

#### Distribution grid data during peak load

A typical daily load profile for a 10/0.4 kV 1000 kVA transformer was taken into consideration for this case. In figure 4 abscissa axis shows the time in hours and minutes, and the ordinate axis shows the current load in kW.



Fig. 4. Typical daily load profile of 10/0.4 kV transformer presented in kW

As can be seen from this profile, the load peak is at 18:30 and is approximately 325 kW. The possibility of an operational mode (N-1) associated with possible tripping of one of the transformers must be considered. In such a case, the maximum load that can be allowed per transformer is 70% of the rated capacity (or 546 kW, with the default value of  $cos\varphi = 0.78$  for the distribution grid), since it is not allowed to exceed 140% of the transformer load even in short term operational modes.

Simulation of the part of the distribution grid was carried out in the RastrWin software package. For this purpose, the parameters of a real power grid section of the cable grid in Ostrovnoy district, St. Petersburg, were taken. The names of substations, distribution points, and lines were changed. The load was selected on the basis of daily load profiles for the winter period and was set in accordance with the daily load peak. Thus, the distribution grid was simulated during peak load in the evening.



Fig. 5. Distribution grid feeder model during peak load in RasrWin

After the number of EVs plugged in the grid during evening peak load has been found, their load is added to the existing load in the nodes. Based on the operational mode calculation results, the conclusion is made about the presence or absence of overload and the presence or absence of an unacceptable voltage drop in the load nodes.

#### Stochastic load from EVs on distribution grid feeder modelling

Due to the fact that most of the currently published works use normal distribution to describe the behaviour of EVs, this paper will firstly consider this method of modelling for later comparison.

Input data for such model are:

- the total number of EVs in use by residents of houses connected to TS, located on this feeder;
- the initial operational mode and configuration of the grid;

- charging type (fast or slow);
- the average speed of EVs in the city;
- normal distribution parameters for travel time and charging time of EVs.

Using these data, this model calculates the number of EVs plugged in the power grid at peak load and calculates the probability of an unacceptable voltage drop.

In our case for the first test of our model 175 EVs were used. The average speed in the city was chosen to be 40 km/h (based on a maximum of 60 km/h), the parameters of normal distribution were chosen based on the average travel time in the city, which is 60 minutes, as well as the fact that most people come home from work around 6.30 pm and immediately plug in their EV. All the charges were considered to be slow level 2 charges with charging power of 22 kW.

These data were used for simulating the model in MATLAB. As it was found earlier, 63000 iterations are enough for accurate result, so that is the number of random iterations to simulate that were used in the model.

The received probability of an unacceptable voltage drop in the consumer load nods is  $P_{drop}=0.6455$ .

It should also be noted that the dependence of the probability of voltage drop on the number of EVs is very sharp. A small change in this amount of EVs has a very strong influence on the resulting probability. For comparison, calculations were made for 165 and 185 EVs. For these numbers of EVs the probability of unacceptable voltage drop was 0.1095 and 0.9589 respectively.

As it was shown earlier, the bootstrap method is more accurate compared to the normal distribution, so it was used for modelling.

Since real data were used for modelling, less additional data are needed compared to normal distribution modelling. The input data in our model are:

- the total number of EVs in use by residents of houses connected to TS, located on this feeder;
- the initial operational mode and configuration of the grid;
- charging type (fast or slow).

With these data, using the algorithms described above the model selects the EVs plugged in the power grid during peak load and then randomly distributes the load from these EVs to all TSs. The modelling results are voltage levels in every node for each of the Monte Carlo method iteration. From these data it is possible to find the probability of an unacceptable voltage drop in consumer load nodes, which is calculated as follows:

$$P_{drop} = \frac{N_{success}}{N_{iterations}} \tag{4}$$

here  $P_{drop}$  is the probability of an unacceptable voltage drop in consumers' load nodes,  $N_{success}$  is the number of iterations in which there was an unacceptable voltage drop,  $N_{iterations}$  is the total number of iterations used in the Monte Carlo simulation.

For the test calculation of this model 200 EVs were taken, the charging power was chosen to be similar to the previous calculation, which is 22 kW. This number of EVs is commensurable with the number of vehicles owned by residents of houses connected to all TSs on the feeder. Probability of voltage drop at consumer load nods is  $P_{drop}$ =0.7278. For illustrative purposes, families of voltage level graphs were plotted. Figure 6 shows voltage levels for each of 63000 iterations.



Fig. 6. Voltage levels in the feeder nodes for 200 EVs and 63000 iterations

For this case a calculation for comparison has also been made, this time for 190 and 210 EVs. The received results are similar to the previous calculation using the normal distribution, namely strong dependence of voltage level drop probability on the number of EVs. Thus, for 190 EVs  $P_{drop}$ =0.2996, and for 210 EVs  $P_{drop}$ =0.9272.



Fig. 7. Voltage levels in the feeder nodes for 190 EVs and 63000 iterations



Fig. 8. Voltage levels in the feeder nodes for 210 EVs and 63000 iterations

It could be seen on Figures 6, 7 and 8 that with the increase of EVs number the average of voltage levels decreases. Same result could be seen in calculations of probability of unacceptable voltage drop.

Additional calculations were made to determine the number of EVs that will lead to probability close to 0 and close to 1. Thus, for 170 EVs  $P_{drop}=0.0042$ , and for 225 EVs  $P_{drop}=0.9957$ .

The results show that different methods of modelling give different levels of accuracy. However, it is safe to say that the real-life data-based method is a more accurate one, as it was shown that the real-life data is not normally distributed. The combination of Monte Carlo method and the Bootstrap method allow us to determine the probability of unacceptable decrease of voltage quality. Obtained probability takes randomness and uncertainties of input data into consideration and evens it out with the usage of the Monte Carlo method.

#### CONCLUSION

In this article various methods of modelling stochastic load from EVs to the distribution grid have been considered. Using various probabilistic estimations and tests, real data on the movement of EVs were analysed, and a conclusion was made that the most frequently used modelling of stochastic load using normal distribution is inconsistent with real data. In this regard, an alternative bootstrap modelling method was proposed, which is the closest to the real data and therefore to the real life movement of EVs. One of the real feeders in Saint-Petersburg power grid was used for simulation, the probability of unacceptable voltage drop on this feeder was assessed.

The results showed that probability has a strong dependence on the number of EVs, and therefore even a small change in the number of EVs leads to a sharp change in the probability of voltage drop. Also the results of two modelling methods were compared. It was shown that when the bootstrap method is in use, compared to using normal distribution, more EVs are needed for unacceptable voltage drop. For normal distribution method probability of 0.9589 was obtained for 185 EVs whereas for bootstrap method probability of 0.9272 was obtained for 210 EVs. It was also found that there is a sharp dependence of voltage level drop probability on the number of EVs which means that even the slightest increase in number of EVs will lead to a close to 1 probability of overload. As a result, it is safe to assume that the usage of the bootstrap method allows some savings in operating reserves since this method is more precise and close to reality and it shows that a larger fleet of EVs is needed for an unacceptable voltage drop.

The described simulation method could be applied to find solutions for unacceptable voltage drop problem, as well as determine the most effective one. For example, Vehicle-to-Grid technology and usage of multi-tariff price scales could significantly increase the number of EVs that could charge in the same district. Such solutions could be modelled with higher accuracy using real-life data and the Bootstrap method.

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## SUBSYSTEM FOR SYNCHRONIZATION AND ANALYSIS OF ARDUINO PLATFORM SENSORS DATA

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#### ABSTRACT

Smart energy systems use Arduino sensors data as the main part. Communication between the Arduino platform sensors and the server is provided by the developed subsystem of messages and serialization to a byte stream. The developed subsystem provides a flexible data transmission mechanism based on the RUDP protocol. This allows us to make the delivery's reliability and confirms packets of specific sensors data, better than systems with TCP or UDP protocols. For example, a system based on TCP protocol can synchronize messages frequently, therefore the acknowledgment mechanism loads network bandwidth. The reliability of a system with UDP will not be provided so UDP requires additional checks. RUDP protocol solves these problems so it was used in our work. Subsystem requires the usage of a Wi-Fi access point from the agent side. Dynamic calculation of the round-trip-time (RTT) was implemented. This value is significant to calculate the time to receive confirmation from the server for each message that needs to be sent or resent. This reduces the number of network errors of data retransmissions and further reduces the load on bandwidth as a result. So, the developed subsystem provides quickly and reliably delivering of sensors data than before. The subsystem can be used in a smart house.

**Keywords**: sensor data synchronization, agent, Arduino board, UDP usage problems, packet delivery reliability, RUDP

#### **INTRODUCTION**

The efficiency of client-server applications ensures their use in various fields. For example, they are used by smart energy systems for the physical synchronization of sensor data as well. Physical synchronization of data uses an Arduino or ESP board and is required to process and store the received data by the server part.

The Transmission Control Protocol (TCP) and User Datagram Protocol (UDP) are widely known transport layer protocols for the physical data synchronization. However, there are problems with the use of these protocols [1], namely fast-changing data in real-time systems. Usage of one of these protocols is a negative for the stable application work and increases the risk of data losses.

This work's aim is to develop a subsystem for real-time systems (namely "Smart energy systems") for data synchronization. The subsystem will ensure the efficiency of the UDP protocol, TCP reliability and uses Reliable UDP (RUDP) protocol [2] to solve the problem.

The tasks of the developed subsystem, which consists of a server and a client on the side of the Arduino board with sensors, are reading data specified by the system user; reliable transmission of messages between the server and the client using sockets for work according to the RUDP protocol; ensuring the most optimal delivery of messages in case of packet loss.

The implementation of the RUDP network protocol in the subsystem solves network problems with packet delay, loss, and duplication in the most optimal way during real-time synchronization of sensor and server data and reduces the load on bandwidth.

#### SUBSYSTEM DESCRIPTION

Smart energy systems belong to real-time systems and are based on control with a highreliability level of technical characteristics of processes [3]. In the literature, there are general approaches to the construction of such systems using some protocols for data transmission [4]. However, unlike systems with streaming video, which have already been explored [5], in the literature, there is no description of real-time systems, which includes the smart energy systems using the RUDP protocol.

Therefore, the developed subsystem will provide real-time smart energy systems efficiency and reliability based on the RUDP protocol.

The architectural basis [6] of the subsystem - client-server. This architecture encompasses distributed systems that involve client-server interaction. A simpler form of the client-server system - a two-tier architecture. It is usually a server application to which clients connect through requests. The server has authoritarian access to the information and provides it in response to requests. An example of this architecture is a GUI application for exchanging data with business logic (database or dedicated server).

In the developed system communication between the server and the client is adjusted at the expense of a subsystem of messages. The key difference between the client and the server here is the processing of different types of messages and different approaches in work preparation.

The developed system was performed using ESP 8266 Nodemcu v3. Wi-Fi libraries were used to transfer data from the ESP card (or Arduino). The ESP8266 module can operate in access point mode and workstation mode, as well as in both modes at the same time. Typically, the access point has a network connection and provides Internet access to the device. Multiple workstations on a local network can communicate through an access point. Each device has its own unique 48-bit MAC address on the network.

To distinguish one access point from another, they have a network identifier called the Service Set Identifier (SSID), a network name that is up to 32 characters long.

In Fig. 1 shows a BME280 test sensor which was used to obtain data on humidity, temperature and atmospheric pressure. In particular, the temperature measurement range with the sensor is from -40 to +85 °C with an accuracy of 0.01 °C.

The sensor supports two interfaces - I2C and SPI [7], in particular, SPI was used in the subsystem. SPI - serial peripheral interface - is a full-duplex synchronous serial communication protocol used for short-distance communication. Since the reliability of data transmission is a priority in the context of the developed system, the choice is based on the I2C ("Inter-Integrated Circuit bus") protocol usage - a two-wire serial protocol for connecting low-speed devices [8].



Fig. 1. Example of a connected BME-280 sensor

To work with the sensor you need to install libraries – Adafruit BME280 Library and Adafruit Sensor. To flash the ESP board in the Arduino IDE, you need to find the appropriate library esp8266 by ESP8266 Community.

After connecting the BME280 sensor to the Arduino board, the BME280test from the Adafruit BME280 Library was downloaded and used as the basis for the interaction.

The subsystem was developed using the C ++ programming language [9] in conjunction with the Qt Framework. Qt Creator – a cross-platform tool for both the preparation of the prototype and at the stage of developing the final product for the user. Qt Framework has a mechanism of signals and slots [10] which are handlers and are connected to the signals. Signals are thrown from a certain class which contains the declaration of this signal.

#### ARCHITECTURE AND SOFTWARE IMPLEMENTATION

The architecture of the created subsystem is shown in Fig. 2. The main application window (MainWindow) is both an element of the system layout and graphical interface. The Network layer module is responsible for network operations, socket manipulation, transmission, packet reception, and data synchronization. The Network layer module combines TCP, UDP, RUDP protocols appropriate for the client and the server. The Network layer module interacts with the Message Subsystem which encapsulates serialization/deserialization of data. The Network layer sends data as an array of bytes over the network. The Agent connects

to the server and synchronizes the registered data. The Server is responsible for receiving data from the client and transmitting it to the GUI (graphical user interface, MainWindow UI here) module. This is done through the built-in Adapter which is an intermediary between the UI and server logic, ensuring the reliability of the multithreaded system (the server is made in a separate thread).



Fig. 2. Subsystem architecture

Fig. 3 shows a sequence diagram of the subsystem. After the client preparation described above, the next step is to configure the server, in particular, the port that the server will open for listening, network protocol, and data retrieval. On the agent side, the developed library is connected, the user configures the name and password to the Wi-Fi-point which will be used to gain access.

Next, determine the code that will be used by the system to obtain data from the sensors and synchronize with the server. The reliability of the message to be synchronized, the sending interval and the flag to synchronize the sensor data at once after confirmation by the server are selected. The client sends the registered data in the form of a reliable message to the server. The agent then turns on, the client sends a request to connect to the server and receives a response, the connection is established. Then the sending of data begins in the set interval (by default - 2 seconds). The server receives these messages, sends updates to the GUI to display them, and adjust as needed. The server has the ability to configure such parameters without source code compilation of the agent board: the specified interval time, reliability (message type), data synchronization enabling flag of a particular sensor. All serialization logic is hidden from the user, but the user within the serialization can describe the appropriate methods for their message types.

The interface of the developed library for Arduino/ESP boards is designed intuitively. The messaging subsystem between the client and the server is designed using the Factory Method pattern.



Fig. 3. Sequence diagram for the subsystem

Serializing messages involves checking for the existence of an object and calling the serialize () method for a specific type of message that returns the number of written bytes.

After deserialization, the message is processed by the system. To do this, a corresponding handler class based on the Singleton pattern is created to have single access to the data of this class.

The server and the client only register certain messages for processing. For example, there is no need for the client to handle messages to the server connection request because the client sends it (server-side should process it).

#### SUBSYSTEM WORKING MECHANISM

The WinSock2.h library is used to work with sockets on the Windows platform. For address and port binding bind () function is used, and send() (for TCP) and sendto() (for RUDP) methods are used to send data. To obtain data recv() and recvfrom() [11] were used. There are no special problems with sending data from the client or the server. However, the data acquisition mechanism is blocking by default which creates a problem even for a multithreaded system. For example, server logic is suspended if it tries to retrieve data from a client. The server and client part which are responsible for network interaction is made in a separate thread of execution to handle it.

It should be understood that recvfrom() calls are used to receive messages from a socket (regardless of whether it supports the actual connection). The recv() call is usually used only on the socket that establishes the connection (for example, TCP).

If the socket does not receive the current packets, recvfrom() calls to wait for a message to arrive and block the execution of the process if the socket is blocking.

The usage of select or poll approaches can be used to receive more data during the determined time.

At each step of updating the server or the client part, the system calls the recvfrom() function and checks if the socket contains any data. If there is no data to process, the sleep instruction for the current stream (server-side) is executed for 5 ms. If there is data, we check

whether all the data for the current packet is received and pass the binary data for further conversion into the appropriate form.

The recvfrom() function returns any available data without waiting for the specified number of bytes required by the user for a single argument to the function. This leads to the fact that during the implementation of the stream logic for message serialization in the developed subsystem using a pointer offset, an error was received on the side of the board ESP8266. ESP8266 has restrictions on access to data through the pointer. Namely, 32-bit access must be aligned beyond the 32-bit limit and 16-bit access must be aligned beyond the 16-bit limit. To fix the LoadStoreAlignmentCause error you need to read or write data to a 32-bit-aligned address [12].

In the proposed subsystem this is solved by using the memcpy function(), which performs low-level copying of data without casting the data to a certain type (via a pointer). The function has the following signature: *void* \* *memcpy* (*void* \* *destination, const void* \* *source, size\_t num*). The function accepts pointers to void, the function does not need to know the type the user is working with, but only knows the *destination* memory address, which must be filled with *num* bytes from the *source* memory.

Additionally, a template thread-safe queue is implemented for requests for the server. There are such requests as suspend/shut down the server, send messages. This queue is checked by the server on each update call and, if requested, processes before receiving the data.

RUDP delivers packets with the organization of two queues (for "reliable" and "unreliable" messages) and separate serial numbers for both of them, respectively. Because RUDP adds logic that controls reliable delivery, receipt, the information about the message is processed first, followed by the message itself.

A "reliable" message will be sent until we receive confirmation of receipt or the limit of available attempts is exceeded, and therefore it is necessary to keep them for some time. Also, messages with a broken order must be buffered before processing the program.

If an "unreliable" message arrives during synchronization, we set its index as the current one on the client or the server-side. To ensure the relevance of the data ignore messages whose index is less than expected (a packet that was sent later has already been received).

Because the system has two main execution threads with a graphical interface and the server separately, a processor with at least two cores is recommended. The system requires up to 15 megabytes of RAM.

To work with the server, run the file ServerApplication.exe and click Start Server. You can then run the agent.

The interval for sending agent sensor data on the client-side can be updated in the Sensor Interval field during server-side work.

When the client is running, the sending time is calculated for each message that the client resends. If in the first step time is equal to round trip time (RTT), i.e. sending occurs immediately, then the resending time is calculated by the equation:

$$T = RTT(2^n - 1)$$
(1)

where n is the number of the current attempt to resend the data packet. That is, the client increases the sending time exponentially and thus reduces the load on the network.

#### **RESULTS AND DISCUSSION**

The simulation of the developed subsystem is performed using the software application Clumsy, which causes such network problems as delay in input in milliseconds, the percentage of lost packets that are sent/received, the percentage of the duplicate packets, and lost order for received and delivered packets. During the simulation, the subsystem work was compared using the proposed RUDP protocol and the known TCP protocol. While modelling in the software application Clumsy, duplication of packets was set to 5%, and simulation of packet loss - in the range of 15-30%.

The simulation results are shown in Figure 4. As can be seen from Fig. 4, for the TCP protocol, the maximum value was obtained when simulating the values of the time spent at 6.22 seconds to simulate packet loss of 15% (Fig. 4 a).



Fig. 4. Simulation of the average waiting time for packet loss of 15% (a, b) and 30% (c)

The results show that during this subsystem work and network parameters simulated by the application Clumsy, packets arrive. To compare performance, the subsystem also simulates work using the RUDP protocol for the same network parameters simulated by the Clumsy application. The simulation results are shown in Fig. 4b, 4c. The figure shows that the subsystem model using the RUDP protocol received a maximum value of time spent 2.03 seconds for simulation of packet loss of 15% and 3.35 seconds for simulation of packet loss of 30%.

That is, based on the simulation, it was found that the maximum value of time spent by the subsystem using the RUDP protocol is three times less than using the TCP protocol. In particular, under the above simulation conditions, the value of time spent by the subsystem is 2.03 seconds - for the RUDP protocol and 6.22 seconds – for the TCP protocol, and therefore in the future, only the RUDP protocol is used for data transmission.

Fig. 5 shows an example of the execution of the server part of the subsystem with data transmission over the RUDP protocol. In real-time mode, the following values were obtained from the sensors: temperature 24 °C, relative humidity 43%, the last received with an interval of 2 seconds was a message with an index of 31. The maximum data waiting time was 2.01 seconds without simulating packet loss.

Also, in the described subsystem, according to formula (1) exponentially set the retransmission time for each message if the subsystem loses the packet. The results of modelling the work of the subsystem in this situation are shown in Figure 6. Fig. 6 shows that the packet -262 is resent at intervals of 0.15 seconds. After this packet is not received, it is resent after 0.35, 0.75, 1.55, 3.15 seconds, which corresponds to the time calculated according to formula (1), where RTT = 0.05.

MainWindow			-	×
Options				
⊖ TCP	art Server Stop Server	Pestart Server		
		Kestalt Server		
RUDP				
MAX elapsed tin 2,01 ÷ Elapsed time 1,45 ÷	ne			
Message id	Temperature	Humidity		
] [	24	ЧЭ		
	Sensor interval			
	Update interval			

Fig. 5. Execution example of server part of the subsystem

That is, the total number of retries for the packet - 262 is 6, and in total, the number of delivery attempts was set in the range of 5-8. After all, attempts are exhausted, the packet is considered lost and the other side of the subsystem is inaccessible.

handleHeartBeatTimeout:	need	to	resent	packet	-	262	interval=0.15
handleHeartBeatTimeout:	need	to	resent	packet	-	262	interval=0.35
handleHeartBeatTimeout:	need	to	resent	packet	-	262	interval=0.75
handleHeartBeatTimeout:	need	to	resent	packet	-	261	interval=3.15
handleHeartBeatTimeout:	need	to	resent	packet	-	262	interval=1.55
observeSendingMessage -	reliable						
Sending result:24							
handleHeartBeatTimeout:	need	to	resent	packet	-	263	interval=0.05
handleHeartBeatTimeout:	need	to	resent	packet	-	260	interval=6.35
handleHeartBeatTimeout:	need	to	resent	packet	-	263	interval=0.15
handleHeartBeatTimeout:	need	to	resent	packet	-	263	interval=0.35
handleHeartBeatTimeout:	need	to	resent	packet	-	263	interval=0.75
handleHeartBeatTimeout:	need	to	resent	packet	-	262	interval=3.15
handleHeartBeatTimeout:	need	to	resent	packet	-	263	interval=1.55
WiFi connected							*

Fig. 6. Example of packet loss and retransmission in a subsystem

#### CONCLUSIONS

Based on the analysis of the literature, it is established that the TCP protocol is used to implement real-time systems.

The developed and implemented subsystem for the Smart energy systems use the RUDP protocol.

The implemented subsystem consists of an Arduino library for an agent board and a server application with a graphical interface. The subsystem encapsulates the logic of data serialization and their sending taking into account the alignment of data addresses, which facilitates the work of the user and the developer with further support of the code. The operation of the described client-server subsystem is to synchronize sensor and server data.

The subsystem is simulated using an application that simulates packet loss during transmission, duplication, and disorder. As a result of the simulation, it was found that the maximum value of time spent by the subsystem is 2.03 seconds - for the RUDP protocol and 6.22 seconds - for the TCP protocol, and therefore in the future for data transmission used only the RUDP protocol.

In case of packet loss due to unstable network work, the subsystem exponentially increases the time of resending packets. In general, the number of attempts to resend packets did not exceed 8.

Thus, the developed and implemented subsystem provides stability and reliability of the Smart energy systems using the RUDP protocol.

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## OPTIMAL DEMAND SIDE MANAGEMENT MODEL BASED ON THE INTERNET OF THINGS

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#### ABSTRACT

The rapid development of renewable energy sources and electricity storage technologies is further driving the change and evolution of traditional energy systems. The aim is to interconnect the different electricity systems between and within countries to ensure greater reliability and flexibility. However, challenges are faced in reaching it, such as the system control, the power grid complexity and the diversity of user needs. To achieve optimal synergies between supply and demand, we need to select and apply innovative solutions and an appropriate control approach. The aim of the control approach is to increase the system efficiency and smooth the load through flexible generation planning and dynamic pricing. The concept of Demand Side Management (DSM) is rapidly developed in many countries and has been named as the future of the energy industry, while its application is part of the transition to smart grids. Introducing DSM in the electricity sector brings huge economic and operational benefits to the power grid. Smart grids include both technology and social factors, such as consumer attitudes towards demand in relation to prices. Demand Side Response (DSR) is both a social solution for smart grids and a new market for users and generators/suppliers. The electricity grid digitalization in the market also requires the installation of smart devices to enable real-time information exchange between the generator and the user. Power generators receive information about users and their habits, while the structured information is used to apply the DSR programmes. The rapid spread of smart grid technologies such as the Internet of Things (IoT) and the Internet of Energy (IoE) ensures communication and reliable development of the power grid infrastructure.

To overcome the challenges of power saving and management, an optimal DSM model based on IoT is basically needed. Unlike other studies and surveys that focus only on the analysis of DSM programmes, this study focuses on a comprehensive assessment of DSM and DSR programmes. Moreover, it presents practice from foreign countries and provides smart grid technologies and tools for an optimal DSM model.

**Keywords:** Demand Side Management (DSM), Demand Side Response (DSR), electricity storage, Internet of Things (IoT), Internet of Energy (IoE), renewable energy source, system control, Smart grid

## NOVEL PARTIALLY INSULATED MULTIPORT DC-DC CONVERTER WITH PARALLEL OPERATION TECHNIQUE

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#### ABSTRACT

This study presents a new partially insulated multiport DC-DC converter topology for photovoltaic (PV) powered battery buffered DC-Microgrid systems. The challenging problem due to their intermittent nature of PVs is eliminated by batteries controlled with the existing H-bridge converters. The input ports are operated in parallel. The proposed converter provides more power transfer by connecting PV arrays and batteries in parallel form. The isolation between the input and output ports is provided by a multi-winding high-frequency transformer (HFT). The primary side of the multi-winding HFT is equipped with individual H-bridge converters for each PVs while the secondary side is endowed with a bridge rectifier circuit. The proposed converter makes it possible to charge batteries in addition to provide power transfer towards the loads. Besides, the proposed converter also allows power transfer from batteries to loads. In order to meet the control objectives of maximum power point tracking (MPPT), battery constant current (CC) / constant voltage (CV) charging and phase shift, a control scheme that includes multi-control loops is suggested. The performance of the proposed converter has been evaluated for different operating modes. In this manner, the viability and the effectiveness of the proposed method have been validated.

Keywords: Multi-port DC-DC converter, H bridge, Photovoltaic, Battery, Multi-loop control scheme

#### **INTRODUCTION**

Nowadays, investigations on renewable energy systems are increasing day by day to reduce the carbon footprint in the world. Since intermitted nature of renewable energy systems (RES), they are often equipped with energy storage units. RESs are widely used in DC-Microgrid systems and electric vehicles because of the advantages of pollution-free and less-maintenance features. PV panels, wind turbines, and fuel cell units are widely used types of RESs.

The output voltages of RESs are not predictable as they depend on natural conditions. For this reason, Energy Storage Unit (ESU) is required in RES-based systems in order to provide uninterrupted power to the loads. Advances in RESs have also accelerated with the developments in power electronics, which enable the flexible operations of power systems as in electric vehicles, grid-tie PV inverters, distributed generation systems. Recently, several studies have been performed regarding the integrated power electronics converters used in a system with multiple RESs or storage units. Fig. 1 shows the conventional micro-grid systems that are endowed with multiport converters (MPCs) [1]–[5] are frequently used in these types of applications.



Fig. 1. Conventional Multiport Converter

MPCs are categorized into three different subclasses as fully isolated [6], [7], partially isolated [8]–[10], and non-isolated [11]–[13]. In fully isolated multiport converters, all ports are galvanically isolated from each other in the system. This type of converters are used in high-power applications that require insulation. In partially isolated multiport converter topologies, all ports in the system are not isolated from each other, but have isolated ports and are used in medium power systems. In non-isolated systems, there is no isolation between all ports and is used in low power systems.

Traditionally, individual ports are endowed with separate DC-DC converters in order to regulate the power flow as illustrated in Figure 1. Recently several studies have been performed in order to develop integrated power electronics converters that are able to integrate multiports. The developed topologies are usually have been formed using the variations of bridge topologies [14-16]. In the proposed study, a converter that can provide high and continuous power transfer by reducing the cost is presented. The proposed multiport converter is illustrated in Figure 2 consists of two H-bridge converters, full wave rectifier and PV/battery units. The isolation between the ports is provided by a high-frequency transformer with two primary and one secondary windings. The h-bridge converters which interfacing the load and PVs shares the switches of S1/S2 and S5/S6 with the integrated bidirectional buck/boost converters interfacing batteries and PVs. Thus, the proposed system integrates four input ports and one output port with a reduced switched structure. In the proposed topology, batteries act as an energy buffer. In the states that the PV panels are not able to produce the demanded power from the loads, the batteries feed the loads in order to provide unintermittent power. When the PV panels produce more than the desired power from the loads, the excessive energy charges the storage units. In this paper, a new partially insulated multiport bidirectional DC-DC converter topology and control method which is used for each H-bridge converters independently to provide uninterrupted power flow have been proposed.



Fig. 2. Proposed Multiport Converter

#### **TOPOLOGY DESCRIPTION**

The proposed converters perform bidirectional power flow in battery side, whereas it performs unidirectional power flow in PV and load sides. The power flow direction of PV is designed as unidirectional because of the nature of PVs. The operation modes of the proposed system is described in two different operating modes. In the first operating mode, the PV panel produces more than the desired power from the loads. In this context, the excess energy produced in PV panels is stored in batteries. The bidirectional buck/boost converter shown in Fig. 2 operates in buck mode. Thus, it reduces the PV panel voltage and charges the battery voltage. In the second operating mode, the PV panel cannot meet the required power from the loads. In this case, the energy required to keep the DC bus voltage constant is met from the batteries. Bidirectional buck / boost converter operates in boost mode.

Fig. 3 shows the control method of the proposed topology. In the proposed control method, two different control methods are used as phase shift and duty cycle. S2 and S6 switches are commonly used in both control methods.



Fig. 3. Proposed Control Methodology

Phase Shift Control Method aims to regulate the output voltage. The output voltage regulation is implemented by phase shifting between the legs of each H-bridge converters on the primary side of the transformer. In other words, phase shifting is performed between the leg

where the S1 and S2 (S5 and S6) switching elements are located and the leg where the S3 and S4 (S7 and S8) switching elements are located. In addition, the high and low side switches of each leg are triggered complimentary. The switches S3 and S4 have a constant duty cycle (50%), while duty cycle values of S1 and S2 switches are determined by MPPT (maximum power point tracking), CC (constant current)/CV (constant voltage) control methods. In order to extract the maximum power from PV, traditional perturn and observe (P&O) MPPT method is used because of ease of operation and reduced computational load. When the MPPT control method is activated, the controller monitors the output voltage of PV and computes the instantaneous available power. The algorithm perturbs the operating voltage by regulating the duty cycle. CC/CV charging algorithms are essential for long service life of batteries. In addition, in the state that the power flow from PV to battery, the bidirectional buck/boost converters operate as buck converter since the PV voltage is more than the battery voltage. When the related system operates in buck mode, the duty cycle value of S1 is equal or below 50%.

#### **Charging Mode**

The excessive power of PVs is transferred to the batteries using MPPT, CC or CV control methods considering the amount of transfer power. For high charging power conditions, the controller uses CC/CV charging algorithms to regulate the charge current sof batteries. Otherwise, the MPPT control method is used to extract the maximum power from PVs.

CC / CV control method operates considering state of charge of the battery. The battery is charged with the allowable maximum current (0.5 C while C represents the nominal capacity of the battery) until battery voltage reaches the threshold voltage value in CC control method. The CC control method is followed by the CV control method, and battery voltage is set to the a constant value while the charge current gradually decrease to 0.005 C. During battery charging, the buck/boost converter operates in buck mode and the duty cycle value of the S1 switch is operating below 50%.



Fig. 4. Power Flow Direction in Charging Mode

#### **Discharging Mode**

The MPPT control method is activated during battery discharge. PV panels generate energy depending on the irradiance the ambient temperature. The irradiation value of the solar panels during the day is constantly different. In this direction, the instantaneous energy obtained from PV varies continuously, as the radiation absorbed by the PV panels change. The MPPT control method is required in order to extract the maximum power from PV. The MPPT control method

ensures that the power obtained in certain periods is sent to the load by following the peak value. In addition, since the battery feeds the loads in discharging mode, the buck/boost converter operates in boost mode.



Fig. 5. Power Flow Direction in Discharging Mode

#### SIMULATION RESULTS

In order to validate the effectiveness of the proposed topology, a simulation study has been carried out on MATLAB / Simulink. The parameters of the topology are given in Table 1.

Two different case studies have been performed. The load power is determined as 5000W in all operations modes. In the results shown in Figure 6, the power of PV Panels has been determined as 1500W. Thus, the power generated in the PV panels is sufficient in the DC-Link and the power will be transferred from the batteries to the DC-Link. In addition to the phase shift control method, the MPPT control loop from the duty cycle controls is activated and the output voltages of the PV panels are fixed. In the simulation results shown in Figure 7, the power of the PV panels is determined as 7500W. Thus, the power generated in PV panels is transferred to DC-Link and batteries. At this point, the CC/CV control loop, one of the duty cycle control methods, is activated as well as the phase shift control method. The batteries will be charged with a maximum charging current up to the maximum voltage value and will continue to be charged with constant voltage after reaching the maximum voltage.

Parameters	Value
PV Maximum Power	10kW
Maximum Power Point Voltage	435V
Maximum Power Point Current	22A
Nominal DC Bus Voltage	350V
Battery Nominal Voltage	200V
Battery Maximum Charged Current	15.5A
Switching Frequency	20kHz
Batteries Inductor	1.5mH
Output Inductor	50uH
Output Capacitor	1mH

Table 1	Parameters	of the	Matlab	Simulink	/Model
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Fig. 6. MPPT Loop Simulation Results

The performance of the system has been investigated under the state that individual PV powers are 1600 W. During the 0-0.2 s time interval the PVs power are not sufficient to meet the power desired from the load. Thus, it is not possible to keep the DC link voltage constant with only PVs. As shown in Figure 6, the PVs are buffered by batteries and power can be transferred to the load without interruption. In this operating mode, in addition to the phase shift control for DC link control, the duty cycle control with MPPT to extract the maximum power from PV is enabled.

After the time second 0.2, the irradiation of the PVs are increase and the available power of the each PV also increased to the 6100 W. In this case, the power of the PV panels meet the power consumption of the load. The excessive power of the PVs charge the batteries. In this operating mode, in addition to the phase shift control method as before, the MPPT control loop is enabled because of the limited battery charging power.

In the simulation results shown in Figure 7, individual PV powers are 7000W. Thus, the power generation ratings of PVs are sufficient for the power demanded from the loads. excessive power of the PVs charge the batteries. During the related time interval, the MPPT control method is disabled because of the excessive charge power is higher than the limits of batteries. Therefore, one of the duty cycle control methods, the CC / CV control loop, and also the phase shift control method are activated. Batteries are charged with maximum charge current up to the maximum voltage value. The CC control method is followed by the CV control method, and battery voltage is set to the constant value while the charge current gradually decrease.



Fig. 7. CC/CV Loop Simulation Results

#### **CONCLUSION AND DISCUSSION**

All renewable energy sources powered systems provide power generation and transmission depending on natural conditions. Being affected by natural conditions poses a problem for loads / dc microgrid networks that require continuity. Energy storage units are frequently used in order to eliminate the aforementioned drawbacks of the renewable energy sources. The integration of battery units are performed by an additional converters that is able to control the power flow of it. Thus, the cost and the control complexity matters reveal. To overcome the related problems several research works have been conducted to develop MPCs.

In this paper, a new partially insulated multiport DC-DC converter topology and control method has been proposed. The main superior aspect of the proposed system is integrating four input ports and one output port with reduced switch converter topology. Also, the proposed converter is a suitable topology for adding more ports by increasing the windings located on the primary side of HFT. Besides, the proposed system performs the control scheme which contains CC/CV charging, MPPT and DC-Link control.

The proposed converter excels with the reduced switch topology. While traditional topologies use individual converters for each ports, the proposed system performs port interfacing via an integrated converter. By the way, the cost, computational load and control complexity of the overall system is reduced. The proposed converter is good candidate for cascaded PV powered and battery buffered applications among the existing MPCs.

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# **CONFERENCE PAPERS**

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## **REFORMS AND CHALLENGES IN GEORGIAN ELECTRICITY MARKET: IMPLEMENTATION OF EU DIRECTIVES**

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#### ABSTRACT

Electricity market-based reforms have been promoted over the past years to improve the Georgian power sector's performance. Relations between Georgia and the EU gained momentum after signing the Association Agreement. The agreement and its core part, a Deep and Comprehensive Free Trade Area, aim to deepen political and economic relations between Georgia and the EU and gradually integrate Georgia into the EU Internal Market. On October 14, 2016, the Energy Community Ministerial Council unanimously approved Georgia's accession to the Energy Community treaty. The country joined as a full-fledged member in 2017, following the ratification of the accession agreement by the Georgian Parliament. Accession requires Georgia to take on obligations set out in the accession protocol, with implementation deadlines, which drives the country into immense reform. The paper analyses undergoing reforms in Georgia and the challenges faced by the country's institutional and legal environment compared to the EU directive's requirements on the electricity sector, especially for the implementation of spot markets. Directive 2009/72/EC of 13 July 2009 on common rules for the internal market in electricity and regulation 714/2009 on conditions for access to the network for cross-border exchanges in electricity is reviewed below, implementation of which is a compulsory condition under the Association Agreement. The paper furthermore analyses the major problems of the country and the ways how to address them.

Keywords: Association Agreement, electricity market model, cross-border trading, reforms, spot market

#### 1. INTRODUCTION

Since its independence from the Soviet Union, Georgia underwent numerous energy sector reforms, ranging from privatization and unbundling previously vertically integrated energy sector entities to creating new public institutions, including an independent regulator. 'Government's non-transparent involvement in various potentially competitive activities leaves a broad area for external influences. This includes electricity and gas imports, subsidization and cross-subsidization of electricity and gas prices, non-transparent agreements signed for new generation project development, and capacity allocation practices.

Market liberalization process in Europe took many years and went through several phases. Energy packages adopted by the EU aim at creating an integrated European energy market, property division, regulation, cross-border cooperation, and the issues of market opening. In the process of liberalization of electricity markets, European states applied different approaches proceeding from their market structures since the implementation of the directive requirements is related to the difficulties. Established on the characteristics of each commonwealth, some may require allowing exceptions.

The third energy package of directives establishes common rules for the generation, transmission, distribution, and supply of electricity, together with consumer protection provisions, with a view to improving and integrating competitive electricity markets in the Community. It lays down the rules relating to the organization and functioning of the electricity

sector, open access to the market, the criteria and procedures applicable to calls for tenders and the granting of authorizations, and the operation of systems. It also lays down universal service obligations and the rights of electricity consumers and clarifies competition requirements.

After joining Energy Community, Georgia took an obligation to set up and comply with the treaty, driving to significant reforms in the sector [8]. On the other hand, reforms are inevitable for 'country's further development to satisfy increasing demand with competitive market instruments. Figure 1 shows that during the last 5 years, yearly electricity consumption outraced electricity generation, which is mainly compensated by imported power, and besides the growth of new generation capacities, there is still a growing gap between supply and consumption [3].

With the ongoing wave of reforms, there is an opportunity and necessity to address as much of these accumulated problems as possible. However, the major underlying problem lies in the lack of strategic vision in the society on importance of energy sector and its place within the frame of the national security. Hence the neglect of its basic needs and problems that finally affect various aspects of 'country's security and sustainable development.

The country has abundant hydropower, wind, solar, and biomass potential and a big number of interested investors that are willing to invest in the sector, and all this requires a competitive and transparent legislative development. There is a strong presence and involvement of the international donor community in the country, and it gives hope that reforms will be implemented in a secure way.

The aim and the objective of the paper is to outline the major challenges that Georgia is currently facing during the energy sector reforms. Structural reforms are very sensitive, and their implementation in a proper way will lead to the growth of investment in the energy sector and thus supporting sustainable and profitable future.



Fig. 1. Electricity Generation and Consumption Rates (GWh)

## GEORGIA AND COMPLIANCE WITH ENERGY COMMUNITY TREATY: GAP ANALYSIS

Energy deficit in member states requires developing an action plan or/and other appropriate documents. After signing Energy Community Accession Protocol, Georgia took certain obligations to implement defined Directives in a given period of time. Beneath are the requirements under the directives and the illustration of the respective situation in Georgia:

For the construction of new generation capacities, member States shall adopt an authorization procedure, which shall be conducted in accordance with objective, transparent

and nondiscriminatory criteria.

Legal framework to attract investment in the power generation sector has been evolving over more than a decade. In 2006 the Parliament of Georgia adopted the State Policy for Energy Sector – a declaration from the Parliament and the Government that the main policy priority was the utilization of 'country's renewable energy potential [4]. This state policy was followed with the first legal basis for the project implementation introduced in 2008. The policy framework was frequently changing over the past years, with 3 different government ordinances regulating the rules for initiation, construction, and commissioning of power plants. Furthermore, more than 20 amendments were introduced over the years in this framework [7].

Despite, frequent changes major steps for initiating and building the power plant have remained the same. The Government of Georgia publicized the list of the potential power plants on which the developer could have expressed interest and submitted the proposal for the project development. In case several developers submitted the proposals for the same projects the bidding took place, in which winner was announced either based on the amount of submitted bank guarantees, proposed Power Purchase Agreements ("PPA") price, or 'Ministry's assessment of the proposal (the rules for identifying the winner have changed several times over the years). Afterward, negotiations with the Ministry took place on conditions of the Memorandum of Understanding ("MoU") and the respective PPA. After signing the MoU and having the framework for cooperation, the investor had to prepare all required documents for permits, licenses, and land rights. At the end of power plant construction, another licensing procedure took place for the power plant to be connected to the grid and to be allowed to sell electricity on the market. Furthermore, the developers could have identified the potential project themselves as well, in which case they should have sent the notification to the Ministry's, that they are conducting the feasibility of the project. After completion and submission of the feasibility study to the Ministry, the developer was allowed to either directly negotiate the project development without any further expression of interest procedures or requested for the project to be added to the 'Ministry's list. In the last case, the developer had an opportunity to be remunerated for the costs of the feasibility study in case the project was developed.

Newly built hydro power plants ("HPP") were granted priority access to the new crossborder 400kv line connecting Georgia and Turkey; Export capacities are allocated based on the following priority groups [6]:

- a. Electricity export/import in emergency situations;
- b. Renewable power plants built since 2010;
- c. Export of power plants built before 2010 and import.

In the event bids from priority groups exceed the 400kv 'line's transmission capacity, capacity is allocated through special auctions arranged by the dispatcher - GSE. Satisfaction of the next priority group starts only after complete satisfaction of the previous priority group. When available capacity is not enough to meet the requests of the certain Priority Group, insufficient capacity should be allocated through the special auction; If any capacity user is unable to provide full utilization of capacity allotted to it, the dispatch licensee makes reallocation with the special auction keeping with the order of priorities. Besides this priority for newly built power plants, due to reduced wholesale market prices in Turkey, Georgian power producers prefer local sales and do not exercise the right for export.

Meanwhile, from 2018, the Georgian Government implemented a new law on Private-Public Partnership, that has to promote renewable project development in the country. However, the lack of support mechanisms hindered project development and very few projects are under development.

Three basic options of Unbundling of transmission systems: unbundling transmission system owners, designation of transmission system operators, and assignment of

independent system operators; Three transmission companies operate in Georgia: Georgian State Electrosystem ("GSE"), owned by 'Georgia's Partnership Fund, has the largest transmission network, including all the major 220/110/35kv overhead lines and strategically important 500kv substations. GSE is the only one dispatch license holder in the country. SakBusEnergo – The Russian-Georgian joint venture owns the 500kv transmission line that

SakRusEnergo – The Russian-Georgian joint venture owns the 500kv transmission line that crosses the entire country and connects Georgia with Russia.

Energotrans, a 100% subsidiary of GSE, owns the 400kv OHL Meskheti line with HVDC back-to-back substations, which connects Georgia with Turkey. The project was completed in 2013 under the framework of the Black Sea Transmission Network project.

Since GSE does not own all transmission lines it operates, it has concluded an operational agreement with these two transmission licensees Sakrusenegro and Energotrans on the Transfer of rights on operation, planning, and development of transmission networks owned by these transmission Licensees. GSE also holds a dispatch license and acts as the Transmission System Operator ("TSO"). Transmission tariffs are set by the regulator. The tariff is based on energy transferred and is not distance related. Legally GSE satisfies unbundling requirements, and it has undergone certification procedures.

One of the requirements to the transmission system operator is to prepare a **network development 10-year plan.** It should be mentioned that GSE has been preparing this plan for the last 5 years.

Granting and managing **third-party access** implies nondiscriminatory access of the parties except when it lacks the necessary capacity to meet technically and economically justified criteria. New power plants often have to upgrade the distribution grid, when connecting to their network. Although the Regulatory commission has set a strict price for connection to the network, there is no other regulation assigning rights and obligations of the parties in order to avoid the subjective approach by distribution companies to new users and generating undertakings;

**Designation of distribution system operator**, which may be functioning under transmission system operator if it has not enough own resources. Legal and functional unbundling is compulsory when it has more than 100 000 consumers and/or is a small isolated system. Market opening requires unbundling of the electricity distribution companies and the introduction of domestic competitive traders. Unbundling of distribution companies is already regulated under existing legislation. Generation and distribution companies formed part of the same vertically integrated company in Georgia. As far as the electricity is traded by long term bilateral contracts, buyer often buys electricity from their own generators. The company Inter RAO UES holds shares of transmission, distribution, and generation companies, while JSC Energo-Pro Georgia holds assets of distribution and generation companies and is building a transmission line.

Under the current model, the distribution companies own, maintain, and operate the electricity distribution systems. They also supply power to end users and small to medium enterprises/industries. In order to introduce a competitive electricity market, it is necessary to separate the retail electricity supply function from the license 'holder's distribution function. Maintenance and operation of distribution systems shall be performed by the existing Distribution Companies, and retail electricity supply shall be performed by retail Public Supplier. The relevant legislation is under development at the moment, and it is very important to secure this transition in a smooth and transparent way so that consumers' rights were protected in the best way.

**Market opening** for promoting competition in the internal electricity market. All large non-household consumers should have free choice. In Georgia market is open for all users.

However, they have to satisfy some technical criteria, and since 2019 some consumers have an obligation to trade on the wholesale market. Before pushing consumers to the market, besides a free choice, there were only a few big consumers participating on the market. As existing market rules require, the cheapest energy first goes to distribution companies, and direct consumers often rely only on carrying electricity, and its price, especially in the winter period, exceeds the sales price set by a regulatory commission. In order to avoid a risk of unnecessary expenses companies do not consider coming on the wholesale market.

Under the current model JSC Electricity System Commercial Operator ("ESCO") buys and sells balancing electricity and guaranteed capacity to satisfy (to balance) the demand of qualified enterprises. The ESCO itself trades about 20% of the wholesale power and is responsible for balancing electricity trade as well as for the guaranteed capacity.

Electricity tariffs for HPPs built before 2008 and with an installed capacity of over 40 MW are regulated. The electricity generated by these HPPs fully satisfies summertime consumption. In the winter, 'Georgia's electricity generation shortfall is bridged by thermal power plants and imports. Electricity prices for newly built HPPs (built after 2008) and all HPPs with installed capacity below 40 MW are fully deregulated.

Establishment of the independent market operator as foreseen under third energy package, responsible for energy balancing services, operating the market will enable [1,2]:

- Setting more transparent rules for the operation of the market operator;
- Establishment of day-ahead scheduling;
- Implementing balancing and settlement rules;
- Introducing hourly/daily settlement;
- Establishment of competitive trading.

-

The regulatory authority shall help to achieve high standards of universal and public service in electricity supply, contributing to the protection of vulnerable customers. This shall include e.g. postponement of payment, etc. In this regard, the regulatory authority has set so-called social tariffs. However, this may be regarded as the harmful practice of manipulating tariffs. This is not an efficient tool, especially when it comes to the protection of the socially vulnerable population. Moreover, there often are cases when the solvent population enjoys these benefits.

Georgian National Energy and Water Supply Regulatory Commission ("GNERC") is very active in drafting and approval of new secondary legislation, also, new Monitoring Rules define huge amount of compliance requirements, therefore, here is a legitimate question, whether the GNERC will efficiently deal and execute its monitoring and regulatory functions not increasing their capacity.

**The increasing role of regulatory authority in the management of internal market.** There is some progress in Georgia in this matter; in particular, regulatory body has been reckoned new function of market monitoring. Activities need to be enhanced in this regard so that the independence and professional level of the regulatory body is increased since a strong regulatory body constitutes grounds for long-term stability and the improvement of the investment climate. It is noteworthy that Georgia meets EU basic requirement – independence of regulatory authority, which is provided in the directive;

**Facilitate cross-border cooperation** to secure the supply of all energy sources at competitive prices. It is necessary to develop specific mechanisms of compensation for the excess of transmission and set harmonized principles for cross-border trade prices and distribution capacity. Georgia has a separate document for relations with each neighboring state. Among them are agreements with Turkey on cross-border trade and interconnection,

providing for capacity distribution on the new Black Sea transmission line. Significant projects were implemented during a recent decade in terms of developing cross-border contacts, including the Black Sea regional transmission line, within which Gardabani – Akhaltsikhe, Zestafoni – Akhaltsikhe, and Akhaltsikhe – Turkey border lines were rehabilitated/constructed, and 500 kW substation (with DC insert) was constructed. Also, construction of transmission trunk line with Azerbaijan was finalized, and construction of "Kazbegi" transmission line with Russia is underway. Rehabilitation and restoration of high-voltage sub-stations are regularly carried out to ensure the uninterrupted and reliable provision of electricity. However, several items need to be implemented:

- In order to foster cross-border electricity trading and attract investments in this sector, bilateral contracts (1 year) have to be shifted to day-ahead market ("DAM");
- Changes in Cross Border Electricity Trading Agreement and the Interconnection Operations Agreement to allow simultaneous bidirectional trade, daily capacity allocation, and price zone trading;
- Market coupling would ease and foster regional cooperation.

Beside the approval of new legislation documents, the country still lacks special regulation on cross-border trading in compliance with new Market Model. This represents the huge problem for planning, especially for those operating export/import business, as risks cannot be adequately assessed for the trading.

**Establishing the European Network of Transmission System Operators (ENTSO-E).** This organization elaborates and establishes network codes, ensures coordination of network operations. Georgia will have to make a lot of effort to join the organization. Notably, Georgia is introducing the regulations which are applied in ENTSO-E member states.

On the other hand, Georgia is facing the following characteristic problems:

- ✓ Georgia has no land border with EU member states. However, it is possible to export electricity via Turkey;
- ✓ The existence of vertically integrated undertakings in the power sector and the MoUs signed with the Government conflicts with the EU principles. In addition, under the MoU export to Black Sea transmission line is planned for many years ahead, whereas in EU member states, cross-border power distribution is never planned for more than one year;
- ✓ The issue of power supply to 'Georgia's conflict areas. More than 45% of 'Georgia's power generation accounts for Enguri and Vardnili power plants, located in conflict areas, which creates a threat to unimpeded and secure electricity supply;
- ✓ The EU allows certain member states (with small, isolated, dependent on one supplier system, or/ and where implementation of any provision prevents system operation, or/and may cause serious economic and financial losses) to apply for exemption from certain obligations. In particular, this refers to unbundling, third-party admission, open market requirements etc.

#### NEW MARKET DESIGN PROPOSED

Besides the pandemic situation all over the World, the Georgian Government decided to push reforms and introduced a new Electricity Market Design in April 2020, the document defining new market participants [9]. Below the Fig. 2 shows a scheme for electricity trading within a new market design. The concept introduced Public Service Obligation ("PSO") producers, Wholesale Public Service Organization ("WPSO"), trading with PPA capacities), large consumers, competitive suppliers, traders, over the counter ("OTC"), universal service supplier and supplier of last resort. DAM and balancing market shall be introduced from July



1, 2021 and relevant procedures for testing and preparation are already in place.

Fig. 2. Scheme for Electricity Trading within New Market Design<sup>1</sup>

According to the new Market Design all PSO power plants, PPA producers will mandatorily sell their generation on DAM, and on the other hand, Universal Service Supplier, Supplier of Last Resort, and the Abkhazian Region, will buy the power on DAM. There will be OTC market as well and buyers and sellers will have an opportunity to trade there as well as on DAM. All deviations from nominated power and actual physical generation/consumption will be subject of imbalance and Balancing Market will provide service for it.

WPSO will trade on DAM on behalf of PPA producers, however the latest will have a choice to participate on their own, and in this case take full responsibility on imbalances. All PPA producers have a fixed price in order to integrate this power on DAM, the Government introduced Contract for Difference ("CfD"). Therefore, PPA producers will receive a fixed price and the price increments during trade will be compensated by WPSO or paid to WPSO. The Government plans to introduce Intra Day Market ("IDM") after 1 year from opening DAM.

Other market participants such as large consumers, competitive suppliers, traders, exporter and importer companies will be able to trade on OTC market as well as on DAM. Each entity is subject tom imbalance and there is not any exception for any company. On the initial stage of the reform, imbalance responsibility might result in huge financial costs for company imbalances as Georgia has a very poor planning experience for power plants as well as for consumers.

Besides the fact that the major stakeholders are working hard to fully implement reform and simulations are run by Balancing Market and DAM, it is very unclear what can be the imbalance cost and how to predict spot prices, as existing new Market Rules do not set up clear bidding strategy for it [10]. This requires running more and more simulations on DAM and Balancing Market close to real situations. However, this will need more time and shows necessity of postponing the spot market opening, as market participants are not adequately informed and educated for such changes.

<sup>&</sup>lt;sup>1</sup> <u>https://genex.ge/en/TabbedPage/Index/60?pageId=60&parent=63&activeMenu=112&activeChild=0</u>

#### CONCLUSIONS

Besides the Government's effort to foster reforms in the country, Georgia is significantly behind schedule. While most of the primary legislation have been approved, as well as a substantial portion of the secondary legal acts, the reform process has stalled due to the lack of adopted primary legal framework.

There is a number of circumstances and reasons which have cumulatively resulted in delays in the energy reform process. First of all, it should be noted that the scale of the reforms ensuing from the obligations is unparalleled. Namely, Georgia had only 18 months, since apporval of new Law on Electricity and Water Supply, to completely restructure both its wholesale and retail electricity markets, establish a new legal framework for regulating renewables and introduce a whole legislative package on the subject matter. The allocated period of time was clearly not sufficient, even considering the additional one-year period foreseen by the Accession Protocol for testing and adjusting the relevant implementing provisions and market instruments.

The establishment of a market model adjusted to Georgian conditions, to meet competition and unbundling requirements requires more time to assure secure market design. Quality assurance and quality control system for the secondary legislation should be designed and implemented including wide discussions with the private sector and non-government sector, donor community, and participation of Energy Community, and each decision shall be justified with respective cost-benefit analysis.

The most important item nowadays is to develop a better incentive mechanism for additional capacity building, including both the additional cost of electricity produced and tax incentives and competitive tenders announced by the government. It should be emphasized that electricity market liberalization in Europe took place in stages, which required three packages of respective energy directives. Georgia will have to pass all these stages needed for final reforming. However, a thorough evaluation of such decisions, scrutiny of each 'requirement's cost- effectiveness need to be carried out prior to making specific steps to their implementation.

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## INCORPORATING VEHICLE AGE DISTRIBUTIONS INTO TRANSPORT MODEL WITHIN MESSAGE ENERGY PLANNING MODEL

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#### EXTENDED ABSTRACT

#### **OVERVIEW**

Ambitious climate change mitigation targets require well calculated action plans as the costs are immense. Energy planning models have been used for the development of such action plans since the seventies. However, primarily for power, heat sectors and fuel supply, neglecting the interrelations with the other sectors. This approach becomes no longer sufficient if we are to expect a rapid electrification of other sectors, especially the transport sector as it affects not only the overall electricity demand but also when it is consumed. Furthermore, smart electric vehicle charging potentially could be used for partial balancing of variable electricity generation from renewable energy sources. Even though, there is a need for multi-sectoral modelling approach, the incorporation of transport sector into the energy planning models is rather uncommon and most of the models that do include the transport sector lack the necessary detail. This paper describes how transport modelling in energy planning models can be improved using vehicle age distributions.

#### **METHODS**

Typically, vehicles in energy planning models are modelled by technologies that consume fuel to produce travel. Separate travel demands are set for each vehicle type. To enable transport modal shift H.E. Daly [1] proposed setting travel demands based on distance (short and long-distance travel) and setting a fixed travel time budget, which is based on idea that people on average spend 1.1 hour travelling per day. In this approach, vehicles additionally consume time from the travel time budget. In this paper, representation of vehicles not only by type and fuel but also by build year is proposed as improvement to previously mentioned transport modelling approach. Vehicle differentiation by build year allows a more detailed vehicle fleet description, potentially resulting in better representation of fuel shift, fuel consumption and in turn emissions. To have realistic vehicle age distribution a set of constraints should be used, which specify how many passenger kilometres have to be travelled by vehicles made in certain years. This is especially important for small, less wealthy countries that have access to large foreign used vehicle age distribution. Two models were created using the same data set of Lithuanian case to compare the results of traditional (H.E. Daly) and proposed approaches.

#### RESULTS

Modelling results using both approaches give somewhat similar results. However, the transition to petrol cars and later to electric vehicles also changes in emissions are more gradual in the proposed approach. Interestingly, electric vehicle penetration is higher in long-distance travel when using traditional approach and in short-distance travel when using the proposed approach. The biggest difference is in emissions, which seems to be too low in the model with traditional approach. This can be explained by the use of single efficiency rate in technology that represents both old and new vehicles of certain type and fuel. In this case, efficiencies of new vehicles were used. Of course, it is possible to adjust the efficiencies so that fuel consumption/emissions would match the statistical data and externally calculate how it should change throughout the modelling years to match the shifting vehicle age distribution. However, most likely it would require more work than to implement the proposed approach.



Fig. 1. Distance travelled in MPkm by different transportation modes and CO2 emissions from passenger road transport using traditional and proposed modelling approaches

#### CONCLUSIONS

- 1. Transport sector modelling in energy planning models can be improved by differentiating vehicles not only by mode and fuel but also by build year. It helps to improve the representation of fuel shift, fuel consumption and emissions.
- 2. In transport models, vehicle fleet age distribution constraints have to be set for smaller and less wealthy countries, which have access to large foreign markets of used cars, because a large share of vehicles taken out of stock is replaced by newer used vehicles instead by new ones.
- 3. The results of models with traditional transport modelling approach and proposed methodology applied were compared. The results show that the traditional modelling approach tends to have very rapid change in technologies while in the model with the proposed modelling approach, the shift is more gradual.
- 4. Even though the methodology was developed within MESSAGE modelling software it is still applicable to most of energy planning models.

#### AKNOWLEDGEMENT

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Keywords: energy planning, transport, model, vehicle, age distribution.

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## COMPARATIVE ANALYSIS OF THE BALTIC STATES NATIONAL ENERGY AND CLIMATE PLANS' POLICIES AND MEASURES FOR INDUSTRY

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#### EXTENDED ABSTRACT

#### **OVERVIEW**

Lithuania, Latvia and Estonia have different industry and primary energy balance structures, but all three states have set ambitious decarbonization goals for 2030. Comparative analysis shows their similarities and the main differences that resulted in slightly different choices for energy transition planned. Since COVID-19 pandemic came into the picture, European Union (EU) considered green recovery path for all of its member states economies, therefore, energy transition process is seen as the best tool to speed up economic recovery [10]. National Energy and Climate Plans (NECPs) submitted to European Commission by EU member states at the end of 2019, describe pre-COVID-19 actions planned to be taken in detail [3, 5, 6, 7]. This paper tries identify the best policies and measures (PaMs) named in the Baltic States NECPs so far, that could be could be considered as the best practices available and replicated.

#### **METHODS**

Comparative analysis concentrates on three official national documents – NECPs and their PaMs for decarbonization goals until 2030 - directly or indirectly related only to the industry within them and leaves energy, transport and agriculture sectors aside. All three Baltic states have prepared different sets of PaMs. It was caused by differences in their energy balances, different energy consumption per capita and unique structure of the national industry sector. Role of national government in ensuring security of supply in energy sector across EU differs [4], therefore, it is safe to assume, that the risk-avoiding countries potentially choose different sets or/and approach to PaMs setting. It is taken into account that EU sees "Green Deal", initially introduced in 2019 [1], and energy transition as the path to its post-COVID-19 economic recovery, so decarbonization goals for 2030 were made even more ambitious in 2020 [2], these chances currently are not reflected in NECPs.

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## DEVELOPMENTS AND TRENDS OF MERGERS AND ACQUISITIONS IN THE ENERGY INDUSTRY

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#### ABSTRACT

Developments, trends, business climate, conditions, factors influencing the efficiency and results of mergers and acquisitions (M&A) in the energy industry are explored in this research. As the business environment is changing rapidly, companies must tailor their strategies in order to survive and grow. Firms may either pursue internal or external growth. Internal growth may be defined as a growth strategy through accumulating profits by management rationalization (e.g. expanding investment, increasing production, improving sales, etc.). On the contrary, external growth is a growth strategy pursued by acquiring some or all of another company's assets. Since 1985, more than 850.000 M&A transactions have been announced worldwide with a value exceeding 67 trillion USD. With a total value of transactions over 9.000 billion USD (13.7%), the energy industry is the second largest industry in the M&A market. On the other hand, statistics show that the energy industry constitutes only 7.2% (over 61.000 transactions) in terms of the number of transactions. Therefore, it results in the situation that by nature M&A in the energy and power industry are double of value in comparison with the average M&A deal. Scientific problem of the research problem addresses developments and trends of M&A in the energy industry. PESTLE analysis and descriptive analysis of sample of worldwide M&A deals in the energy industry were performed in the study. DataStream 5.1 database by Thomson Reuters was employed to identify the sample of global international companies which took over another company in the period 1995-2020. Results imply several findings. First, while role and presence of M&A in the energy industry is increasing, the purpose of the M&A deals has changed remarkably. Second, most M&A events were undertaken to create synergies and cut costs during 1985-2010. Since last decade firms are pursuing M&A in order to find new ways to grow and ensure supply given declining levels of accessible oil and gas reserves, to address growth challenges and gain access to reserve. Finally, PESTLE analysis lists factors which clearly signify that transformation of the worldwide global energy market reflects various changes in the main market parameters.

Keywords: mergers and acquisitions (M&A), energy, development, trends.

#### **INTRODUCTION**

Already 30 years ago Freier (1990) has made an empirical observation that "over the past 20 years, the minimum company size required to compete successfully in most industry segments has been steadily increasing". Within the content of this assertation is a premise that growth is a critical element for business survival and prosperity. Two main paths are leading to business growth. Either companies grow internally by nurturing within-firm resources and internal investments or firms pursue an external growth strategy and proceed with acquiring other firms. Mergers and acquisitions (M&A) may be defined as transactions between two independent companies when a company (merging company or acquirer) buys a business unit or an entire company from another company (merged company or acquired company). Even though the terms merger and acquisition are often used interchangeably, they refer to different agreements and different mode of transactions in practice. A merger occurs when two companies, often of about the same size, agree to go forward as a single new company rather than remain separately owned and operated. Following this transaction, companies' stocks are surrendered and new company stock is issued in its place. On the contrary, an acquisition occurs when a firm takes over another and establishes itself as the new owner. From a legal perspective,

the acquired firm ceases to exists, the acquiring firm absorbs the business and the buyer's stock continues to be traded while the target company's stock does not.

The worldwide energy landscape is undergoing various transformations. While energy needs were modest prior to industrial revolution, the steam engine's evolution during 17th and 18th centuries has opened a world of possibilities. Further, coal powered steam engines, electric generators, hydroelectric plants introduced in the 19th century have enhanced accessible energy capacities. Low cost automobile, spread of electricity, large power plants, massive coal plants, hydroelectric dams, powerlines and nuclear power plants were the fundamental driving forces of energy production and accessibility in the 20<sup>th</sup> century. Cainenga et al. (2016) have reviewed the history of energy use and provided forecasts that sooner or later, oil, gas, coal and new energy sources will each account for a quarter of worldwide energy consumption in the new era, specifically speaking, accounting for 32.6%, 23.7%, 30.0% and 13.7% respectively. Similarly, statistics available on Statista forecasts that worldwide electricity generation is expected to double from 24,77 trillion kilowatt hours in 2018 to 44,26 trillion kilowatt hours in 2050. Most significant is the structural change of renewable sources which are estimated to generate 49% of total electricity generation.

According to the Global Industry Classification Standard (GICS), the energy industry consists of companies that explore, produce, refine, market, store, and transport oil and gas, coal, and other consumable fuels. Many companies in the energy industry have already implemented or are planning to engage in M&A transactions because this growth strategy is known to be quicker and in many cases cheaper than internal development or strategic alliances. However, empirical studies do not provide coincide results and do not unambiguously confirm that M&A transactions generate an economic return. Similarly, an open question remains whether related on unrelated M&A leads to better results. Besides growth itself, M&A transactions in the energy industry seem promising in many cases as they may improve operational efficiencies and analytical capabilities. Issues of operational efficiencies and analytical capabilities are essential and urgent especially for oil and gas companies, because currently depressed prices means that profits are hard to come. On the other hand, they are also essential for renewable energy, which has been quite expensive in some cases, because the infrastructure is not in place.

Two leading schools of thoughts constitute the theory of M&A waves. Firstly, the neoclassical theory is based on efficient market premises. Secondly, behavioral M&A wave theory is based on the non-efficient market premises. Research of several authors have elaborated on the neoclassical theory. Mitchell & Mulherin (1996), Maksimovic & Phillips, (2013) were among scientists who supported that M&A is the reconfiguration of resources whose aim is to improve efficiency in response to the external environmental changes including technological changes and innovation, industry-specific deregulations, economic shocks and so on. From the perspective of neoclassical theory, Servaes (1991), Jovanovic & Rousseau (2002), Harford (2005) have further added that M&A transactions manifest the profit-pursuing nature of capital, as capital flow prefers high-quality and efficient enterprises to low-quality and inefficient ones. Xu et al. (2018) have added that neoclassical theory supports the idea of capital liquidity being the fundamental driving force behind M&A. For instance, according to the authors, the neoclassical theory can only forecast the wave of M&A when the capital liquidity is strong. Shleifer & Vishny (2003), Rhodes-Kropf et al. (2005), Savor & Lu (2009) are among scientists who analysed and supported the behavioral theory. Behavioral theory holds the position that waves of M&A are caused by the stock market's misvaluation and senior executives' opportunistic behaviour.

A study of Harford (2005) has found that regulatory, economic and technological shocks drive industry merger waves. However, according to the researcher, it depends on the sufficient

capital liquidity whether the regulatory, economic and technological shocks would lead to an actual M&A wave. In his empirical research, Harford (2005) has analysed industries with merger waves. Among other findings, it was found out that petroleum and natural gas industry has experienced M&A wave in June, 1997 which was caused by increasing prices, record drilling and increasing costs leading increased size to be more efficient. Similarly, in the utilities industry M&A wave was also found to have occurred in November, 1997. Harford (2005) clarified that the wave in the utilities sector was caused by deregulation in some markets and elimination of a law prohibiting mergers between non-contiguous providers.

In recent years, though the value and volume of M&A in the energy industry have increased, there is a knowledge gap in systematic literature review of developments and trends in the industry especially from methodological and managerial perspectives. The research seeks to overcome this gap and provides a systematic literature review on developments and trends of M&A in the energy industry. The paper's main purpose is to investigate and critically discuss developments and trends of M&A in the energy industry with the focus on M&A dynamics and its driving forces.

Based on previous studies, author conducts a structured literature review to critically discuss and evaluate the developments and trends of M&A in the energy industry. The research is carried out as a structured assessment of past literature. Findings from scientific articles and studies by various researchers have been being categorized, grouped and summarized to discern a meta-analytic view of the work carried out to date.

The rest of this paper has been structured as follows. Section 2 provides research background and literature review on consolidation in the energy industry to better understand industry M&A. Section 3 provides results of PESTLE analysis and elaborates on the worldwide outlook of M&A with a focus on dynamics, volume, geographical scope and diversification perspectives. Concluding remarks and directions for future research are outlined in Section 4.

#### CONSOLIDATION IN THE ENERGY INDUSTRY

Looking from historical perspective, the energy industry has evidenced several shocks and consolidation waves caused by geopolitical decisions, fluctuating oil prices, low economic growth and transaction cost of upstream and downstream divisions in the value chain. Reddy & Xie (2017) acknowledge that industry consolidation has been ongoing for over four decades and is still evolving. Firstly, the industry has significantly affected and stimulated the business consolidation activities around the major oil price shocks in 1980s and 2000s. Secondly, the industry has evidenced several large-scale M&A deals as a response to a market-force toward rising crude oil price. Thirdly, the industry has indicated an unpredictable crude oil price signalling in recent years. Price volatility coupled with increasing production costs and negative cash flows, has intensified the market for cross-border M&A transactions in the industry.

Galperina & Klen (2017) have noticed that M&A in the energy sector have industry specific features, e.g. declining levels of accessible oil and gas reserves, non-traditional players (national oil companies (NOCs), private equity firms and oil services companies) jumping into the M&A game, regional consolidation of energy services, drive by governments worldwide to promote renewables growth, etc.

In addition to the external circumstances, it shall be observed that the energy industry's consolidation is also stimulated and M&A therein directly depend on the development of the energy itself, because the development of certain areas of the energy sector establishes an attractive sub-sector for the prospective investor. Accordingly, the transformation of the worldwide energy markets affects the assessment of the attractiveness of the M&A transactions. Furthermore, considering energy industry unique characteristics create unique sources of

synergies, potential M&A synergies in this particular industry needs to be investigated and explored further.

Extending the work of Fraunhoffer & Schiereck (2012), Table 1 presents a value chain of the energy industry regardless of the energy source. The energy value chain may be divided into three segments: upstream, midstream, and downstream. Each segment has specific characteristics which may be utilized during M&A in order to generate synergies.

	Upstream	Midstream	Downstream
Prerequisites for	Scale to lower costs	Asset	Convergence
synergy exploration:	per customer	optimization	between energy
			related services
Synergy objective:	<ul> <li>Scale synergies</li> </ul>		
	<ul> <li>Scope synergies</li> </ul>		
	<ul> <li>Financial synergies</li> </ul>		
	<ul> <li>Operational synergies</li> </ul>		

Table 1. Value chain of the energy industry

Source: created by the author, extending work of Fraunhoffer & Schiereck (2012).

Upstream is commonly known as the exploration and production section. It covers all activities related to searching for, recovering, and producing crude oil and/or natural gas from underground or underwater fields. Exploration and production sector covers the drilling of exploratory wells, subsequent drilling and operating the wells that recover and bring the crude oil or raw gas to the surface. The upstream sector focuses primarily on commodity, low margin, and high-volume aspects and requires scale to lower costs per customer in order to explore synergies. Thus, the focus is primarily laid upon commodity, low margin, and high-volume aspects.

The midstream sector connects the upstream sector to the downstream sector. While midstream operations often include some elements of the upstream and downstream sectors, its main activities consist of transportation (pipeline, rail, barge, oil tanker, and/or truck) and marketing of wholesale products. Within the nature of the midstream segment, pre-requisite to synergy exploration is the focus upon scale with physical assets, to not only reduce costs, but also to do marketing and trade capabilities, which are intended to lead to asset optimization.

The energy industry' downstream sector encompasses refining, transportation to retail facilities and marketing the finished products. The convergence drives the downstream segment between primarily gas and electricity as well as other energy related services.

Using data, provided by Statista, Fig. 1 includes forecast of electricity generation worldwide from 2018 to 2050, by energy source (e.g. liquids, natural gas, coal, nuclear and renewables).



Fig. 1. Projected electricity generation worldwide from 2018 to 2050, by energy source (in trillion kilowatt hours)<sup>2</sup>

#### Source: created by the author, using data by Statista.

When looking into energy generation forecasts in Figure 1, several general trends of world energy development are observed. Firstly, as summarized by Cainenga et al. (2016) energy sources changes from fossil (high carbon) to non-fossil (low carbon). Conventional sources like coal are increasingly being replaced by natural gas, renewables, and nuclear power. This transition implies that market changes reflect demand of green development of ecological environment. Secondly, according to the data, electricity generated by most energy sources worldwide, with the exception of liquids, will increase in the coming years. Total electricity generation is forecasted to almost double from 24,77 trillion kilowatt hours in 2018 to 44,26 trillion kilowatt hours in 2050. Third, electricity from renewable sources is expected to experience the largest growth of up to 21.66 trillion kilowatt hours in 2050, from almost 7 trillion kilowatt hours in 2018. This constitutes a structural change from 28% to 49% of total electricity generation. Overall, current projection foresees increased consumption from all fuel sources, except for coal, where demand seems to have plateaued. Considering trends and changes in electricity generation worldwide, integration of different distribution grids shall be taken into consideration. Badami & Fambri (2019) have established that the increased use of fluctuating renewable energy sources will lead to challenges concerning their full integration in the distribution grid, the reduction of renewable energy sources curtailments and the mitigation of electric imbalances on the grid. Besides electric batteries, other technologies (e.g. Power-to-Gas, Power-to-Heat, Combined Heat and Power) make it possible to exploit synergies between various energy networks, thus alleviating problems of renewable energy sources integration. Overall, when these technologies work simultaneously in a single energy system, their installed power mix, and their optimised management and control, play a fundamental role in the energy optimisation of the whole system.

Moeller, Schlingemann, and Stulz (2004) have identified the transaction premium as a crucial explanatory factor for the bidders and target's revaluation in the M&A transactions. Furthermore, authors have elaborated that synergies and resulting premiums are essential for the success of M&A.

<sup>&</sup>lt;sup>2</sup> <u>https://www.statista.com/statistics/238610/projected-world-electricity-generation-by-energy-source/</u>

Table 2 summarizes findings of studies which found empirical evidence on energy sector synergies for certain energy-related M&A deals. It becomes evident that no universal finding prevails in each study. Fraunhoffer & Schiereck (2012) have performed literature review of empirical studies which analysed M&A synergies in the energy sector. Authors have concluded that financial synergies are of minor importance for energy-related mergers. On the other hand, scale and scope synergies as well as operational ones are of significance and manifest primarily in power generation and distribution functions.

Study	Region	Utility focus	Synergy objective	Findings
Christensen & Greene (1976)	US	Power generation	Scale synergies	Scale economies diminish with increased firm size
Sing (1987)	US	Gas/electricity utilities	Scale/scope synergies	Mean utility firm has diseconomies of scale/scope
Salvanes & Tjotta (1994)	Norway	Electricity utilities	Scale synergies	Scale synergies only for small utilities
Burns & Weyman Jones (1996)	England/ Wales	Electricity utilities	Scale synergies	Evidence for scale economies for all utilities
Filippini (1996)	Switzerland	Electricity utilities	Scale synergies	Economies of density for small/medium utilities
Yatchew (2000)	Canada	Electricity/ water utilities	Scale/scope synergies	Scope synergies are suggested for small utility firms
Fraquelli, Piacenza & Vannoni (2004)	Italy	Gas/electricity/ water utilities	Scale/scope synergies	Small utility firms display economies of scale/scope
Kowka (2005)	US	Power distribution	Scale synergies	Scale economies are conducted
Piacenza & Vannoni (2009)	Italy	Electricity	Scale synergies	Vertical and horizontal scale synergies
Goto, Shang & Toshiyuki (2009)	US	Gas/electricity utilities	Financial synergies	Synergies vanished for multiutilities after deregulation
Goto & Toshiyuki (2009)	US	Gas/electricity utilities	Operational synergies	No synergies for multiutilities
Fraunhoffer & Schiereck (2012)	Germany	Energy providers	Scale/scope synergies	Financial synergies are of minor importance for energy-related mergers. Scale and scope synergies as well as operational ones are of significance and manifest primarily in power generation and distribution functions
Curran & Spigarelli (2017)	EU, China	Wind and solar sectors	Scale/operational synergies	Technology integration and the consolidation of capacities across the supply chain were key motivations.

Table 2. Energy sector synergies for certain energy-related M&A deals

Source: created by the author.

Research of Curran & Spigarelli (2017) concludes that technology integration and the consolidation of capacities across the supply chain were key motivations for M&A deals in the energy industry.

## **KEY CHARACTERISTICS OF GLOBAL MERGERS AND ACQUISITIONS IN THE ENERGY INDUSTRY**

This part of the paper provides the results of the PESTLE and descriptive analyses. PESTLE analysis was performed in order to determine driving forces of M&A in the energy industry. Considering motivation and main questions of the study, sample of M&A deals which have occurred during the period 1995-2020 worldwide has been analysed. DataStream 5.1 database by Thomson Reuters was employed to identify the sample of international companies which took over another company in the period 1995-2020. Furthermore, this database provides deal characteristics (e.g. announcement and completion date, transaction value, initial bidding and target company specific information (e.g. size, the listing status of the target, geographical scope, industries companies are active in, etc.).

#### Driving forces of M&A in the energy industry

Galperina & Klen (2017) have noticed that the transformation of the worldwide energy markets affects M&A efficiency and future from various perspectives. These may be characterized by political, economic, social, technological, legal and environmental factors, which all are being reflected in the PESTLE analysis. According to the PESTLE framework concept, Table 3 below provides analysis of M&A in the energy industry.

Factors	Effect of factors
Political	<ul> <li>Greater political stability paves the way for new forms of cooperation between energy companies and governments, especially in the developing world.</li> <li>Political instability and uncertainty about future reforms in developing countries reduce profits of energy companies</li> <li>Restructuring in the energy sector and stimulating energy development will promote the attraction of new investments and the development of energy companies, which will promote industry M&amp;A</li> <li>Denationalization and privatization contribute to increased investment in energy and the exit of international energy companies into such state's market.</li> <li>State support for the development of renewable energy promotes the development of companies that generate or use it in their activities.</li> <li>The policy of expansion in the external energy markets will promote international M&amp;A</li> <li>Cross border and overseas energy infrastructure control policy will help international M&amp;A</li> <li>Policies of demonopolization in national energy markets increase competition that changes the conjuncture</li> <li>Implementation of sustainable development strategies will contribute to economic growth, and hence to an increase in M&amp;A transactions.</li> <li>Implementation of energy efficiency policy will reduce energy consumption, which will lead to a reduction in the profits of power companies</li> </ul>

Table 3. PESTLE analysis of M&A in the energy industry

Economic	- Coronavirus faces oil companies with the worst oversupply in history
Leononne	Supply pact by OPEC and other producers known as OPEC - collapsed on 6th
	- Supply part by OI EC and other producers, known as OI EC+, conapsed on other March 2020 bestering a drop in prices that were already falling due to the
	March, 2020, hastening a drop in prices that were already ranning due to the
	coronavirus outoreak.
	The economic growth of countries contributes to the growing demand for energy,
	and, accordingly, profits of energy companies increase
	– Low tax rates for energy companies contribute to increased incomes of energy
	companies, and vice versa, high ones contribute to lower incomes
	– Fluctuations in oil prices increase the risk of loss of profits and investment risks
	- Instability in exchange markets boosts the value of energy producing from
	imported primary energy sources
	- The liberalization of the energy markets of developed countries will contribute to
	the increase of M&A transactions.
Social	- An increase in the population contributes to increased demand for energy and
boolar	therefore for the growth of profits of energy companies
	- Increased middle class share in developing countries increases the demand for
	- increased initiale class share in developing countries increases the demand for
	Evelogization of the consciousness of nonulation contributes to the use of
	- Ecologization of the consciousness of population contributes to the use of
Tashralasissi	Intervention of the electricity are duction to the lock of the second state
Technological	- Improvements of the electricity production technologies from renewable energy
	sources will help to reduce the cost and increase profitability in this energy sector
	- The development of deep drilling and offshore oil and gas extraction technologies
	will reduce the cost of electricity production and increase the profits of vertically
	integrated oil and gas companies
	- The development of technologies for the extraction of shale gas, petroleum,
	bituminous sands will reduce costs and increase the efficiency of energy companies
	- The development of hydrocarbon processing technologies will increase the
	efficiency of vertically integrated oil and gas companies
	- The widespread introduction of Smart Grid technologies at all levels (local, on-
	site, regional, national, international) will facilitate optimization of electricity
	supply, which will reduce the expenditures of energy companies
	- The introduction of intelligent technologies and the robotization of certain energy
	companies will increase their attractiveness for potential transactions of M&A
	- Reducing or eliminating the digital divide will facilitate agreements in developing
	countries
	- The introduction of secure technologies by energy companies increases their
	attractiveness for M&A transactions
Lagal	The focus on liberalization of electricity markets in the EU will facilitate the
Legai	- The focus on international energy companies in Europe
	Increasing restrictions can halp to monopolize and increase monopoly profits of
	- increasing restrictions can help to monopolize and increase monopoly profits of
	Strengthening of antitrust laws can reduce the profits of energy companies
	- Strengthening of antifust laws can reduce the profits of energy companies
	- Adjusting of budgeting requirements will increase the efficiency of national
	energy companies in developing countries, which will lead to an increase in M&A
	transactions.
	- implementation of the standards on energy management at the legislative level
	will reduce energy consumption, which will reduce the profits of energy companies
	- Legalization of the energy service will reduce energy consumption, which will
	reduce the profits of energy companies
Environmental	- There is a new focus on sustainable development— developing oil and gas
	resources in ways that will leave a positive economic legacy for those countries
	when their reserves run out.
	- The Paris Climate Agreement on reduction of carbon dioxide emissions dated
	2016 and other environmental programs of the countries will promote the
	development of renewable energy, gas and reduced use of coal as an energy source,

which will increase the share of transactions in the market for the production of
electricity from renewable energy sources
– EU 2050 long-term strategy. The EU aims to be climate-neutral by 2050 – an
economy with net-zero greenhouse gas emissions. This objective is at the heart of
the European Green Deal and in line with the EU's commitment to global climate
action under the Paris Agreement.
- Increased environmental safety requirements to energy companies will increase
their expenses, which will reduce the number of M&A.

Source: created by the author.

Firstly, political factors are governed by the degree of intervention by governments in the economy and they significantly affect the conduct and performance of M&A in the industry. From this perspective, greater political stability, denationalization and privatization, state support for the development of renewable energy, industry restructuring, de-monopolization policies, and implementation of sustainable development strategies greatly affect environment, scope, volume and outcomes of M&A in the energy industry.

Secondly, among critical economic factors are economic growth of countries, tax rates, fluctuations in oil prices and other commodities, instability in currency exchange rates, liberalization of the energy markets. These factors define the future of companies in the energy sector, affect the firms growth strategies and shall be taken into account when analysing current and future prospects of M&A in the energy sector.

Thirdly, increase of global population size, increasing middle class and concerns over ecology are among social factors which shape the M&A deals in the energy industry.

Moreover, technological factors such as improvements of the electricity production technologies from renewable energy sources, the development of deep drilling and offshore oil and gas extraction technologies, the widespread introduction of Smart Grid technologies, intelligent technologies and wide-spread robotization are a few among technological factors which challenge and affect industry M&A.

Liberalization of electricity markets in the EU, strengthening antitrust laws, and implementing standards on energy management at the legislative level are most cited and important legal factors that shape industry M&A deals as organizations must comply with the laws that the legislature has laid down.

Finally, the trending focus on sustainable development, the Paris Climate Agreement on reducing carbon dioxide emissions and globally increasing environmental safety requirements are among environmental factors which shape M&A in the energy industry. The EU aims to be climate-neutral by 2050 - an economy with net-zero greenhouse gas emissions. This objective is at the heart of the European Green Deal and in line with the EU's commitment to global climate action under the Paris Agreement.

Factors listed in the PESTLE analysis clearly signify that worldwide energy market transformation reflects various changes in the main market parameters. M&A decision making, subsequent volume and value of the deals, outcomes of the transactions, etc. all reflect political, economic, social, technological, legal and environmental factors. Most important of these are: fluctuation of commodity prices, increasing oil supply, penetration and active developments of renewable energy sources, employment of Smart Grid technology enabling reduction of transaction costs due to flexibility and work in the optimal mode of electrical grids; liberalization of energy markets in the EU, USA, Japan, South Korea, Australia, etc.

#### Global outlook of M&A in the energy industry

Figure 2 describes the annual deal value and volume of M&A in the energy industry. Several trends may be observed from the statistics. Firstly, 22.428 M&A deals with total value

exceeding 7,016 trillion USD completed during 1995-2020. Secondly, the annual deal value and volume of M&A has fluctuated considerably. While the number of deals has been relatively stable from 1995 to 2001 (702 deals per year), the value of annual deals has increased by over 394 percent (from 46 billion USD in 1995 to over 230 billion in 2001) leading to the average deal size increasing from 82 million USD to 317 million USD. The value of deals has been the lowest from 2002-2004. However, the number of deals per year has doubled in the period from 2002 to 2008. The peak of the annual deal value has been reached in 2007 and exceeded 414 billion USD. Similar annual M&A values have been experienced in 2013 (409 billion USD) and 2017 (403 billion USD).



Fig. 2. Annual deal value and volume of M&A in the energy industry

Source: created by the author, using data by DataStream 5.1 database by Thomson Reuters.

Thirdly, the annual deal value has been relatively stable from 2010 to 2017 and averaged 378 billion USD. However, it shall be observed that number of deals has been decreasing since 2011. According to the data by DataStream 5.1 database by Thomson Reuters on M&A deals worldwide, a critical conclusion may be drawn that average deal value has almost doubled, from average deal value of 307 million USD in 2011 to over 600 million USD in 2020. This raises several concerns. Firstly, reduced number of deals and increased deal value may indicate low number of industry players competing for the market share. Moreover, this change suggests changes in market structure. Secondly, reduced number of deals suggests that companies switch from external to internal growth strategies. Finally, given trends raises concerns on possible overvaluations in capital markets.

Figure 3 distinguishes between domestic and cross-border M&A. Interestingly, while number of deals has fluctuated during 1995-2020, the percentage of domestic deals have stayed relatively stable and amounted to 69.7%. Accordingly, on average 30.3% of the deals have been cross-border and involved bidding and acquired companies from different countries in the said period. However, increased volatility shall be observed in the period of 2005-2008. Specifically, percentage of domestic deals have accumulated to 75.3% in 2005 and went down to 63.8% in 2008.





Figure 4 provides insights into diversifying vs. consolidating M&A in the energy industry. Several trends are being observed. Firstly, 65.3% of the deals completed during 1995-2020 were diversifying. Secondly, while diversifying M&A amounted to 61.1% in 1995, their share had increased to 81.5% in 2020. Thirdly, while the number of diversifying M&A was relatively stable during 1995-2011, a sharp increase of diversifying M&A was experienced in 2012-2020. This trend implies that companies pursue diversification M&A to expand their product and service offerings. Bidding companies believe the unrelated M&A unlocks synergies that promote growth or reduce prevailing risks in other operations.



Fig. 4. Dynamics of diversifying vs. consolidating M&A in the energy industry Source: created by the author, using data by DataStream 5.1 database by Thomson Reuters.

#### CONCLUSIONS

The observation triggered the research that while role and presence of M&A in the energy industry is increasing, the purpose of the M&A deals has changed remarkably. The most M&A events were undertaken to create synergies and cut costs during 1985-2010. Since the last

decade firms are pursuing M&A to find new ways to grow and ensure supply given declining levels of accessible oil and gas reserves, to address growth challenges and gain access to the reserve.

This paper identified and assessed various developments of M&A in the energy industry during 1995-2020. Following conclusions can be drawn from the extensive literature review, structured assessment of past studies and sample of worldwide M&A:

- Even though many companies in the energy industry have already implemented or are planning to engage in M&A transactions because this growth strategy is known to be quicker and in many cases cheaper than internal development or strategic alliances, but empirical studies do not provide coincide results and do not unambiguously confirm that M&A transactions generate economic return;
- Energy industry has been ongoing for over four decades and consolidation is still evolving;
- Value chain of the energy industry may be divided into upstream, midstream, and downstream segments with each seeking to generate scale, scope, financial and/or operation synergies during employment of M&A;
- Ongoing changes in energy sources' nature imply that market changes reflect demand of green development of ecological environment. Increased use of fluctuating renewable energy sources leads to challenges concerning their full integration in the distribution grid, reducing renewable energy sources curtailments and the mitigation of electric unbalances on the grid. Besides electric batteries, other technologies make it possible to exploit synergies between various energy networks, thus alleviating problems of renewable energy sources integration.
- Trending focus on sustainable development, Paris Climate Agreement on reducing carbon dioxide emissions and globally increasing environmental safety requirements are among environmental factors which shape M&A in the energy industry.
- Factors listed in the PESTLE analysis clearly signify that the worldwide energy market transformation reflects various changes in the main market parameters. M&A decision making, subsequent volume and value of the deals, outcomes of the transactions, etc. all reflect political, economic, social, technological, legal and environmental factors. Most important of these are: the fluctuation of commodity prices, increasing oil supply, penetration and active developments of renewable energy sources, employment of Smart Grid technology enabling reduction of transaction costs due to flexibility and work in the optimal mode of electrical grids; liberalization of energy markets.
- M&A in the energy industry dispose waves like tendencies and the cyclical nature of mergers and acquisitions processes development;
- Average deal value of M&A in the energy industry has increased from 307 million USD in 2011 to over 600 million USD in 2020, raising concerns about changing market structures and overvaluations in the capital markets.
- Companies pursue diversification M&A to expand their product and service offerings. Bidding companies believe the unrelated M&A unlocks synergies that promote growth or reduce prevailing risks in other operations.

Future research shall be directed to empirical investigation in this field and direction. It is recommended to perform an actual and country- or region specific study elaborating on developments, changes in market structure, consolidation of energy industry that are circumstanced by increased volume of M&A in the industry.

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## SYSTEMATIC LITERATURE REVIEW ON CORPORATE SOCIAL RESPONSIBILITY IN ENERGY SECTOR

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#### EXTENDED ABSTRACT

#### **OVERVIEW**

Corporate social responsibility (CSR) has gained reputation recently, and energy sector companies started to recognize responsibility for society and the environment. Due to the current changes and increased competition in the energy sector, energy companies could use CSR as a differentiation strategy to handle competitive demands from prosumers and other market players [1]. The corporate social responsibility in energy sector is the main business initiative helping to deal with major risks and challenges associated with climate change and delivering sustainable energy development goals [2]. There are also important risks associated with corruption in energy sector. Measuring and managing the various corporate social responsibility issues can help to provide both energy utilities and investors in the sector with a better understanding of their businesses implications to sustainable energy development and to find answers on how to ensure consumer costs low while shifting to new energy saving technologies and a renewable energy portfolio and mitigating negative environmental impact. CSR reports of energy utilities can't provide assessment of the true impact of energy utilities on the sustainable energy development of the country as assessment of CSR performance of energy companies requires more deep investigations and application of advanced tools. There is a wide array of studies focusing on CSR in the context of the energy industry. Still, there is no agreed framework to assess the CSR of energy sector companies. This paper aim is to develop theoretical framework for addressing CSR issues relevant for energy companies by reviewing literature systematically.

#### **METHODS**

The systematic search and study of literature was carried out in accordance with the framework of the Stochastic Approach for Link Structure Analysis (SALSA) that explores random walks on graphs derived from the link-structure. The SALSA approach allows a potential subjectivity factor to be reduced and is known as one of the most appropriate methods for literature recognition, assessment and systematization. The Preferred Reporting Items for Systematic Reviews and Meta-Analyses (PRISMA) statement guarantees the precision and completeness of the analysis. Table 1 offers the basis for systematic literature search and analysis of this research.

Steps	Explanation		
Search	Key activities: keywords definitions; databases for search.		
	Scope of research: indicators and methodologies for CSR issues relevant for energy		
	sector		
Appraisal	Key activities: papers selection through the PRISMA statement.		
Synthesis	Key activities: data extraction and categorization.		
Analysis	Key activities: analysis of the data, result comparison and conclusions.		

Table 1: The search and analysis process for systematic literature

It is necessary to define the scope of the research before starting the search of the database and to identify the correct keywords that is used during the search process. In the Web of Science (WoS) database, a literature search was carried out on a variety of topics: "Corporate social responsibility in energy sector" + "Corporate social responsibility assessment in energy sector" + "Corruption in energy sector". A total of 113 relevant publications were found during the search based on topics in tittle and abstract. Using

PRISMA statement and snowballing technique, total 36 publications were selected where different indicators and methodologies for CSR issues relevant for energy sector presented or applied.

#### RESULTS

Corporate social responsibility comes in many different shapes and sizes which is demonstrated by many authors. Alexander Dahlsrud [3] specified five primary areas of CSR, namely: environmental, social, economic, stakeholder and voluntariness. Companies wish to successfully develop their activities are forced to engage all key partners into the corporate social responsibility (stakeholder), including all links of the production process, item of providing quality products and services, transparent company management (economic), care of employees (social), environmental protection (environmental) and cooperation with the local community (voluntariness) [4]. While stakeholders identify three main Corporate Social Responsibility issues on which companies from the energy and fuel sector should concentrate: care for the national environment (81%), care for the safe labour of employees (81%), ensuring secure supply of energy (80%) [5]. The corruption risks also play important role in this sector due to its' specific operating environment and the nature of activities taking into account the monopolistic character and the role of state in management boards of energy companies. The drivers of CSR in energy sector are the mix of incentives and requirements. These drivers are market-based or requirement-based, they can be categorized in three groups: economic, social and political drivers [6].

Advanced CSR has been already investigated by several authors, in the energy field as well as in other fields, but a comprehensive framework to analyse the shift from traditional CSR to advanced CSR is not yet available in literature a lot. The main dimensions characterizing advanced CSR are: priority of social and environmental issues; shared value; long-term perspective; integrated planning; innovations; deeper involvement of the stakeholders; active focus to solve the issues affecting community [6]. Other authors use score for CSR strengths where they summed the total numbers of strengths related to the community, corporate governance, diversity, employee relations, the environment and the product. CSR strengths and concerns are often summed and used as a composite measure. But this approach has been criticized in the literature with reason [7].

The cohesive framework created by the Global Reporting Initiative (GRI) and sustainable reporting are used worldwide. European energy sector companies know the GRI Guidelines and use them widely [5]. Further assessment framework development could be adopted according to current CSR practices in the European electricity sector. Using the reporting principles the key criteria could be included in the research structured in three "pillars" – the economic, environmental and social pillars of CSR. The GRI performance indicators are structured in the same way, and most companies follow the three pillars in their reporting structures [8]. All key partners into the CSR (stakeholder) and cooperation with the local community (voluntariness) would be evaluated using "CSR Evaluation matrix". In a multi-criteria, multi-stakeholder perspective, an evaluation of CSR performance for a selected site results in an array of judgements (See Fig. 1) [9].



Fig. 1. CSR Evaluation matrix

As many indicators for CSR are presented and used in the assessments in the literature, this matrix allows to address the central issue of getting the "right mix" of indicators through a process of

stakeholder dialogue involving their interests and expectations. Indicator selection rooted in stakeholder engagement would be one of the most valuable outputs for further assessment framework development.

#### CONCLUSIONS

Corporate social responsibility comes in many different shapes and sizes which is demonstrated by many authors. Advanced CSR in energy sector has been already investigated by several authors and the main dimensions characterized: priority of social and environmental issues; shared value; long-term perspective; integrated planning; innovations; deeper involvement of the stakeholders; active focus to solve the issues affecting community. Other authors use score for CSR strengths where they summed the total numbers of strengths. Assessment framework for CSR in energy sector is related to the Global Reporting Initiative and it's three "pillars" – the economic, environmental and social performance indicators. All key partners (stakeholder, voluntariness) evaluated using "CSR Evaluation matrix". Indicator selection rooted in stakeholder engagement would be one of the most valuable outputs for further assessment framework development.

Keywords: Corporate social responsibility; energy sector; literature review; SALSA.

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## A PREDICTION OF BUILDING ELECTRICAL ENERGY DEMAND BY USING ANN AND SVM

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#### ABSTRACT

After the rising penetration of electricity generated from renewable resources on modern power system in the smart grid era, electrical energy demand prediction has become pivotal for a variety of applications containing building energy planning, management, and optimization. Due to uncertainties in building energy consumption profiles, prediction of electricity demand can be defined as an arduous challenge owing to nonlinearity caused by impacting factors namely, climatic, temporal, economic, social, and random factors. In order to cope with the nonlinearity, machine learning algorithms are frequently employed in modelling electrical energy demand. This paper offers a half-hour-ahead electrical energy demand prediction of 10 Downing Street which is one of the well-known buildings on a global scale because of being the official residence and the office of the prime minister of the United Kingdom. Half-hourly electrical energy demand data of the 10 Downing Street belonging to the year 2017 has been evaluated with calendar and meteorological data to form a data set. In the meantime, machine learning algorithms including artificial neural networks such as multilayer perceptron, radial basis function, and generalized regression neural networks along with support vector machines with linear and radial basis functions have been rigorously applied to the data set for the electrical energy demand prediction of the next 30 minutes. Consequently, results of the prediction are presented by using several performance metrics in detail for comparison. The aim of this comparison is to demonstrate well known method performances on this energy dataset. It has been observed that RBF based applications gave better results.

Keywords: Electrical Energy Demand, Prediction, Artificial Neural Networks, Support Vector Machines, Building.

#### **INTRODUCTION**

In recent years, energy production and utility has become more significant than before. The universe is deteriorated by humans from different perspectives, but especially from ecological balance. Electrical energy demand has increased more than ever with the developing technologies and increasing population. Environmental pollution is intense all around the world and majority of this pollution is caused by developed countries. While fossil resources are gradually decreasing, renewable energy resources become popular.

Nowadays, people are aware of energy efficiency and they try to reduce unnecessary energy consumption for all areas. Herein, short-term electrical energy consumption is a necessity for energy management and planning of all buildings. After the increasing influences of electricity generated from renewable resources on modern power systems especially in the smart grid era, electrical energy demand prediction has become essential for a variety of applications.

Different methodologies are used for predictions. Because of the uncertainties in building energy consumption profiles, prediction of electricity demand may be defined as a tedious challenge due to nonlinearity caused by affecting factors named as climatic, temporal, economic, social, and random factors. In order to cope with the nonlinearity, machine learning algorithms are frequently employed in modelling electrical energy demand. Demand is usually difficult to predict since it is connected to economic growth and demographic expansion [1].

The energy consumption increases with a continuous trend. Energy supply is related rising industrial applications closely. Now, research is focusing on electrical energy demand prediction by combining artificial and statistical intelligence-based methods. Two of the building electrical energy forecasting methods are artificial intelligence (AI) methods such as support vector machine (SVM) and artificial neural networks (ANN). ANN and SVM is used linear and nonlinear data applications. Both are commonly utilized in the field of prediction owing to finding the most accurate approach. Moreover, these methods are widely used in the field of forecasting and their aim on finding the most accurate approach is ever continuing [2].

ANN is one of the methods implemented in different studies for prediction. The use of ANNs in the energy sector has been widely researched. Thanks to their good generalization ability, ANNs have received considerable attention in smart grid forecasting and management [3]. The ANN is defined a data driven approximation. The data is used by ANN to capture the relation between input and output variables and forecast the output values. An ANN is composed of a network of processing nodes (or neurons), which perform numerical manipulations and are interconnected in a specific order. The historical data can be used by ANNs to predict the future [4].

The other technique is SVM chosen and utilized in this study. SVM possesses great potential and superior performance as appeared in many previous research, the results guarantee global minima. SVM can solve some demerits of the neural networks, and has many advantages in minor samples and nonlinear high-dimensional ones [5]. A key feature of SVM is that training SVM is equivalent to solving linear constrained quadratic programming problems. Thus, SVM solutions are always unique and globally optimal. SVM differs from other networks' training which requires nonlinear optimization with the danger of getting stuck into local minima. The process of the problem solution depends only on a series of the training data, which is called a support vector. Use only the support vector to get the same solution as using all training data points [6].

In this study, a short-term electrical energy demand prediction of 10 Downing Street, which is one of the famous buildings over the world, is proposed. Energy supply continuity and planning is very important for this building which is very critical. Because of these, this data is chosen. The data set was created by evaluating the electrical energy demand data of the building for 2017 with the calendar and meteorological data. The data is from 2017 because it is not shared periodically. Artificial intelligence-based algorithms such as multilayer perceptron (MLP), radial basis function (RBF), and generalized regression neural network (GRNN), SVM with linear and radial basis functions have been applied to this data set for the electrical energy demand prediction of the next 30 minutes. Finally, all the results have been shown by using several performance metrics (coefficient of determination, mean absolute error, mean absolute percentage error) for comparison.

After this introductory section, ANN and SVM methods for predicting electrical energy demand are briefly reviewed in Section 2. In Section 3, results are analysed and discussed with their details. Finally, conclusions are presented in Section 4.

### MATERIALS AND METHODS

#### Materials

Material of the study is the data set, which is obtained from [7] [8] and [9]. It includes 17518 rows and 17 columns. These are consisting electrical, meteorological, and calendar data. The data is belonged to 10 Downing Street building. 10 Downing Street ground floor plan is represented in Fig.1[10] [11] to provide an overview for this building.



Fig. 1. Ground floor plan of 10 Downing Street

10 Downing Street which is one of the well-known buildings on a global scale because this building is the official residence and the office of the British Prime Minister. The 10 Downing Street is a specific building for the world because the building dominates the world politics. In the literature, there is a clear gap in predicting the electrical energy demand of such building, which makes this paper special. It is a specific building where energy demand estimation is important, as the slightest problem in the energy supply of this building can cause bigger problems. The data set has 17 input variables. Electrical variable which consists of historical electrical energy consumption along with meteorological and calendar variables constitute the input variables of the data set. Dataset is normalized before the processing step. The details of data set are shown in Fig. 2. Including these variables are important for these types of datasets prediction applications performances. Target is 30 minutes ahead electrical energy demand.



Fig. 2. Flowchart of the data set variables, methods and target

#### **Prediction Methods**

ANN methods are applied for forecasting methods which is defined MLP, GRNN and RBF. In addition to ANN techniques, SVM is implemented. Linear and RBF kernel functions are used because choice of the kernel function is affected the method performance.

#### Artificial Neural Network (ANN)

ANNs are designed inspiring from the biological neural networks. Because of this reason, ANNs contains neurons, weights, and bias. ANNs are most common in the machine learning field. There are many ANN structures used in the machine learning problems, but the MLP is a widespread ANN type [12]. ANN is used to learn the relationship among past, current and future temperatures and loads and electrical demand forecasting [13].

Main advantage of neural networks is providing an extensive range of functional relation between inputs and output. Generally, neural networks work and forecast well despite incomplete, noisy, and fuzzy data. Further, they do not require a priori hypothesis and do not impose any functional form between inputs and output. Because of this, neural networks are practical than the other statistical methods to use where knowledge of the functional form relating inputs and output is lacking, or when a prior assumption about such a relationship should be avoided [14]. MLP is a type of feed forward neural network. The input layer takes the input for processing. The MLP necessary capabilities such as prediction and classification are implemented by using the output layer. Hidden layer number is optional. It is placed in between the input and output layer. The data flows in the forward direction from input to output layer. The back propagation learning algorithm is utilized for training MLP neuron. MLP can solve problems which are separable nonlinear ones. MLP are used especially classification, prediction and approximation studies.

$$o(x) = G(b(2) + W(2)h(x)),$$
(1)

$$h(x) = \Phi(x) = s(b(1) + W(1)x),$$
(2)

with bias vectors b(1), b(2); weight matrices W(1), W(2) and activation functions G and s. The set of parameters to learn is the set  $\theta = \{W(1), b(1), W(2), b(2)\}$ . Typical choices for s include tanh function with tanh(a) =  $(e^a - e^{-a})/(e^a + e^{-a})$  or the logistic sigmoid function, with sigmoid(a) =  $1/(1 + e^{-a})$  [14].

The ANN other method is GRNN. It is a one-pass learning algorithm with a highly parallel structure. It is shown that, even with sparse data in a multidimensional measurement space, the algorithm supplies soft transitions from one observed value to other one. The algorithmic form can be used for any regression problem in which an assumption of linearity is not justified [15]. This technique basic formula is given below:

$$y(x) = \frac{\sum_{i=1}^{n} y_i K(x, x_i)}{\sum_{i=1}^{n} K(x, x_i)},$$
(3)

where y(x) is the predicted value of input x,  $y_i$  is the activation weight for pattern layer neuron at  $i, K(x, x_i)$  is the RBF kernel [16]. GRNN model includes four basic layers. The first one is the input layer which is connected to the second layer. The third layer is a hidden layer which can be called summation layer. This layer has two different nodes. The first one is the sum of the first hidden layer outputs, each weighted by the observed output. The second one is the sum of the first hidden layer activations. The output layer receives the two outputs coming from the hidden layer. Then, the output layer divides them to yield a prediction for y.

The last implemented ANN method is RBF which is defined a type of feed-forward networks. RBFs train by using a supervised training algorithm. RBF networks has only one hidden layer which uses RBF as the activation function. These functions are very powerful and effective in approximation. These types of neural networks have attracted from many researchers because it can be successful for solution of different problem domains. The RBF network usually trains much faster than back-propagation networks. This type of network is less susceptible to problems with nonstationary inputs because of the due to RBF hidden layer units.

$$y(x) = \sum_{i=1}^{M} w_i \, e^{\left(\frac{-(\|x-c_i\|)^2}{2\sigma^2}\right)},$$
(4)

where, x, y(x),  $c_i$ ,  $\sigma$ , and M denotes input, output, center, width, and number of basis function centered at  $c_i$ , similarly  $w_i$  denotes weights [17]. RBF is utilized with Gaussian function. Because Gaussian function tends to be local. RBF is unlike the others, it declines with distance from the center, and forms the classic bell shaped curve which maps high values into low ones, and maps mid-range values into high ones [18].

#### Support Vector Machines (SVM)

Support vector machines (SVM) is a supervised machine learning method. This methodology is applied in many different fields, for instance time series prediction, regression analysis, pattern recognition, etc. SVM are known for the ability to handle high dimensional data. SVM is a type of machine learning algorithm. The SVM follows the concept of separating the features from one another. The classifier separates property from one another. The same types of properties come on one plane, and another property comes on another plane. The classifier is using the concept of the aircraft, lines, and hyperplanes to separate the features. The classifier line for different dimensional data. The human does not describe higher aspects, but the computer can reach there. SVM is best when all the elements are tightly bounded. If the features are not together then this concept does not work correctly [19].

SVM models are similar with multilayer perceptron neural networks. SVM can be used as an alternative in order to train classifiers. It consists of RBF, linear, polynomial, and multilayer perceptron by using a kernel function. In the kernel function, solving a quadratic programming problem, which is related with linear constraints instead of dealing with a nonconvex and unconstrained minimization problem with training the ordinary neural network, determines the weights of the network [20].

Given a set of training examples, each marked as belonging to one of two categories, an SVM training algorithm builds a model that assigns new examples to one category or the other, making it a non-probabilistic binary linear classifier. A SVM maps training examples to points in space in order to maximize the width of the gap between the two group. New samples are then mapped into that same space and estimated to belong to a group based on which side of the space they drop. SVM linear kernel function is given:

$$K(x,z) = x^T z. (5)$$

SVMs can implement a non-linear classification implicitly mapping their inputs into high-dimensional feature spaces by kernel trick. SVM is defined the adjacent data points to hyper-plane. The original maximum-margin hyperplane algorithm proposed as a linear classifier. Then, a new way designed the kernel trick to maximum-margin hyperplanes by using non-linear classifiers.

RBF function for SVM method is given below equation:

$$K(x, x') = \exp(-\gamma ||x - x'||^2), \tag{6}$$

$$\gamma = \frac{1}{2\sigma^2},\tag{7}$$

where x and x' are represented two samples of RBF kernel. Free parameter is represented  $\sigma$ .

#### **RESULTS AND DISCUSSION**

A personal computer with OS version Windows 10, a processor of 2.5GHz (Intel Core i7), and a memory size of 8 GB is used for implementations of this study.

In MLP, search for the optimal number of hidden layer neurons is covered from 2 to 20 neurons. Activation functions are used as logistic for hidden layer and linear for output layer. GRNN is used with Gaussian kernel function.  $\sigma$  value range is determined between 0.001 and 10. Maximum number of neurons is assigned as 100 for RBF. Maximum  $\lambda$  is 10.

SVM is performed with two different kernel functions. These are linear and RBF functions.  $\varepsilon$ -SVR regression model is used, and parameter ranges were between 0.1-5000 for C, 0.0001-100 for  $\varepsilon$  and 10-3 and 0.001-50 for  $\gamma$ .

In this study, energy consumption values are predicted by employing five different techniques. A comparison of predicted values which are calculated by using chosen techniques and actual values are shown in Fig. 3. These values belong to an arbitrary day energy data.



Fig. 3. Actual and predicted values comparison plot

Coefficient of determination  $(R^2)$  mean absolute error (MAE), and mean absolute percentage error (MAPE) are used for comparing performances of applied methods.

Random sampling method is applied training and validation steps for all models. 80% of the data set is employed to constitute training data and 20% of the data set is distinguished to form validation data in a random manner.

Method	Type or Kernel	$\mathbb{R}^2$	MAE (kWh)	MAPE (%)
ANN	MLP	97.09	1.71	2.94
	RBF	97.68	1.55	2.66
	GRNN	98.08	1.37	2.34
SVM	Linear	97.02	1.73	2.99
	RBF	98.02	1.44	2.25

Table 1. Applied methods performances for all utilized metrics.

In Table 1, comparison of R<sup>2</sup>, MAE and MAPE values of different ANN and SVM techniques are shown. It has been shown GRNN is the best one among ANN techniques. On the other hand, SVM RBF method is given the best result between SVM methods. But SVM methods are not well in terms of computational time. Their computational terms are longer than ANN methods.

#### CONCLUSIONS

Electrical energy demand forecasting has gained significance with increasing energy demand. With the increasing need for energy and the misuse of people's resources, nature has been harmed and continues not to be given. Decreasing life of world and energy sources is effective on this situation. But impacts such as climate factors, social activities, and humidity factors make predict future electric loads difficult. So, cope with the nonlinearity, machine learning algorithms are frequently employed in modelling electrical energy demand.

In this paper, a half-hour-ahead electrical energy demand prediction of 10 Downing Street which is one of the well-known buildings on a global scale is presented. As a result of this study, it is considered that GRNN and SVM RBF is recommended because of providing high accuracy within very short computational times.

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## REGRESSION BASED METHODOLOGY TO EVALUATE POWER GENERATION SOURCES INFLUENCE ON ELECTRICITY MARKET PRICE: LITHUANIA CASE

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#### ABSTRACT

These days electricity generation systems are experiencing a substantial change. Environmental goals are decreasing the number of fossil fuel power plants which are replaced by environmentally friendly renewable energy generation sources. In the future, broader introduction of energy storage systems and electrical vehicles will make the electricity system even more complicated. Changes in national electricity generation mix can either decrease or increase electricity price for the end-user depending on the generation costs and grid expenditures. It is important to understand how electricity market price might change by introducing new generation sources to ensure that power is affordable for the residents and industry is competitive. This paper introduces regression-based methodology to evaluate power generation sources influence on electricity market price in Lithuania. Energy system of Lithuania is chosen because of lack of analysis concerning Lithuanian electricity market price and ambitious goals to generate a significant amount of electricity using renewable sources in the future.

The goal of the methodology is to identify long-term regional power generation sources influence on the same region electricity market price. It involves electricity market and energy system statistical time series analysis using correlation and regression methods. To use the methodology statistical data for the electricity market price, load demand and in the region present generation sources should be gathered. The data should be collected for at least five-year time period and transformed into average monthly values. If time series data have structural breaks or other defects appropriate statistical methods should be used to fix issues and ensure final results quality. To select generation sources which meaningfully influence electricity market price two steps correlation method is used. In the first step, correlation analysis between all generation sources and electricity market price is performed. Generation sources with correlation coefficient higher than 0.3 are selected for the further step. In the second step, correlation analysis between electricity load and selected generation sources is performed. Generation sources with correlation coefficient higher than 0.7 are excluded from further analysis. Two step correlation analysis helps to identify generation sources which constantly influence electricity price and exclude the ones which are used only for peak generation and balancing. Finally, linear regression analysis is performed where dependent variable is electricity market price and independent variables are selected generation sources. Regression equation is a final methodology result where coefficients values besides the independent variables show long-term generation sources influence on the electricity market price.

By analysing Lithuanian energy system, eight power generation sources were identified: biomass, natural gas, hydro pumped storage, run of river, photovoltaic solar, waste fuel, wind and electricity import from neighbouring countries. First step correlation analysis revealed that biomass, run of river and electricity import have a higher than 0.3 correlation with electricity market price in Lithuania. Second step correlation analysis showed that biomass generation have a higher than 0.7 correlation with Lithuania electricity system load, for that reason biomass generation was removed from further analysis. Run of river generation and electricity import were selected for the final linear regression step. Regression analysis confirmed that both selected variables have a significant influence on electricity market price. Regression equation showed that 1 MW increase of average monthly run of river generation could decrease electricity market price by approximately  $0.13 \in$  while 1 MW increase of average monthly electricity import could increase electricity market price by approximately  $0.02 \in$ .

Keywords: Lithuania, electricity market price, power generation sources, correlation, regression

# **CONFERENCE PAPERS**

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## LAMINAR BURNING VELOCITY ESTIMATION USING DEEP NEURAL NETWORK

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#### ABSTRACT

When simulating turbulent premixed combustion, a modelling simplifications are often made in order to make simulations realisable at practical scales. One of the main simplifications is omitting detailed chemical simulation and exchanging it with simplified phenomenology based model. Often in order for such a simplified model to be accurate, empirically based correlations are used. One of the critical parameters, estimated using such correlations is laminar burning velocity. However, due to experimental complexity involved with laminar regime of hydrogen combustion, there is no universally accepted correlation for hydrogen-air mixtures.

The purpose of this work is to present implemented deep neural network model for the estimation of hydrogen-air mixture flame laminar burning velocity. While it is still based on experimental data, there is an expectation of accuracy increase from neural network model compared to using correlation. The implemented deep neural network estimates laminar burning velocity based on hydrogen concentration, temperature and pressure of the mixture. The paper details the process starting from data preparation to final results.

Resulting model calculations are compared with correlation results and experimental data gathered from literature and iterated. This model can be integrated with other simulation tools and be used for fast but accurate estimation of hydrogen flame laminar burning velocity.

Keywords: Laminar burning velocity, deep neural network, hydrogen-air mixture

## INTRODUCTION

Modelling simplifications are often employed to make simulations of turbulent premixed combustion realisable at practical scales. The main target of most simplifications is removal or reduction of combustion chemical reactions simulation. Eliminating chemical terms from the combustion model allows to avoid both the equation stiffness due to short timeframes of reactions and a need to address extremely small length scales of flames.

One of the most common ways to avoid chemical modelling is to evaluate reaction source terms with simplified phenomenology-based models, e.g., Turbulent Flame Speed Closure [1 model. Often in order for a such simplified model to be accurate, empirically based correlations are used. One of the critical chemistry-based parameters required for the premixed combustion simulations is laminar burning velocity (LBV) of the simulated mixture. However, for hydrogen-air mixtures there is no universally accepted LBV correlation due to experimental complexity involved with laminar regime of hydrogen combustion [2]. Furthermore, accuracy of currently available correlations is suspect in regions with lower data density since empirical correlations seek to describe results obtained from the entire available multi-parameter experimental range with a single comparatively simple expression.

Artificial intelligence (AI) models have been gaining interest in recent years as the alternative methods to, among other applications in various fields, describe dependencies between application-specific input and output parameters. As such, it seems to be a promising candidate to model experimentally determined dependencies between parameters. Due to the ability of AI

models to account for more complex dependencies, increase of prediction accuracy compared to correlation use is expected.

This work presents development of deep neural network model to predict hydrogen-air mixtures LBV values based on experimental data. The implemented deep neural network estimates laminar burning velocity based on hydrogen concentration, temperature and pressure of the mixture. This work compliments several other recent examples of similar developments by other authors. In [3] ANN model of methane-air mixtures LBV was developed, with pressure, temperature and equivalence ratio as inputs. Similar models were also developed for single-fuel mixtures of normal hydrocarbons C1-C7 with air in [4]. The work concluded not only that ANN model predictions were of satisfactory accuracy, but also noted fast evaluation compared to reaction mechanism calculations. In [5] ANN model predicting LBVs of natural gas mixtures enriched by hydrogen and carbon monoxide at several selected mixture compositions was presented. The results showed high accuracy of predictions. [6] presented ANN for LBV estimation of hydrogen and propane mixtures with air. In this work issue of small sample size was addressed by replacing experimental data with probability density functions based on polynomial approximations of experimental results. [7] presented ANN model predicting LBV of hydrogen-methane-air mixtures. In this work it was shown that accuracy of the developed ANN model was higher than of generalized linear regression, support vector machine or random forest models (based on the same experimental data). Referred literature works show explorative attempts at applying ANN approach for combustion simulations, precisely, estimation of LBV. These pioneering works show good accuracy of results, usually higher than other common methods. This work aims to offer another realization of ANN for LBV estimation with the following considerations:

- the developed model is intended to be used in turbulent premixed combustion CFD solver, this work reports development of the working ANN model itself

- at this stage model is intended for the hydrogen-dry air mixtures of different temperatures, pressure and equivalence ratios

- similar work is presented in [6]. Current work is different from it by 1) wider experimental dataset 2) the ANN model implementation details 3) retention of purely experimental data in the model dataset. We strive to keep closer to the experiments and address issue of small sample size by interpolating additional velocity values between relatively close experimental points. We also use these procedure to give different weights to experimental values of different quality (estimated). More interpolated data points are generated from experimental results judged to be of better quality than from the ones of worse quality. We consider such approach to be beneficial by being more true to experimental values and by being well-suited for constant expansion by new experimental results, where addition of new data allows to redistribute weights of different experiments keeping total sample size similar.

#### **GATHERING AND PREPARING DATA**

The training database for the model was composed from the experimental data available in the literature [6; 8-32]. Experimental LBV values for dry hydrogen-air mixtures at varied temperatures and pressures were used. In order to improve accuracy of developed model, outlier data points were removed from the training database. Remove can be performed with 1.5 IQR method [33]. As Fig. 1 shows, for normal conditions, few of such data points were present from Koroll experiments dated in 1993 [16]. Removing aberrant values prevents this artificial neural network (ANN) from getting uneven and will keep smoothness, which should be close to true values. From the same figure, it is already possible to notice the form which ANN model will try to obtain.



Fig. 1. Experimental data from literature for normal conditions. Data named based on authors [6; 8-32]

During the next step of data preparation, values for other than normal conditions (temperature and pressure) were added. For the training of this ANN model, experimental data in temperature range from 296 K to 450 K and pressure range from 0.1 MPa to 0.5 MPa was used. Also, only data for dry hydrogen-air mixtures is used. Based on the experimental data, the trained model is suitable for the laminar velocity predictions of the mixtures with the equivalence ratio in interval 0.25-5.

Amount of the available experimental data (about 800 data points) was insufficient for an adequate training of DNN. The amount of data was increased by additional points, obtained through the linear interpolation between neighbouring experimental points.



Fig. 2. Correlation plot

Looking at Fig. 2, which shows data Spearman correlation, it is easy to notice that ratio has biggest impact on burning speed, while pressure has negative impact. Taking that into account, to maintain physical adequacy of the ANN model predictions, in this paper we will add few extra values to the training database. Creating a model at this stage and checking the influence of pressure variations in some cases would give negative velocity values in regions near 0 equivalence ratio if model was used out of bounded areas. To prevent such behaviour, database was updated with extra parameters in this work - 0 m/s velocity value at 0 equivalence ratio value and random temperatures and pressures. This way model is prevented from providing nonphysical LBV values at extremely low equivalence ratios.

The final database developed for model training contains over 2000 data points, which include both the experimental measurements and additional values interpolated from them. Such dataset is less accurate than purely experimental, however data simulation was needed due to limited number of experimental data points. This should be sufficient amount of data for ANN to reach satisfactory results. During the next step, the training database was split to the test and train sets. In this paper 20 percent of all data was used for the test set and 80 percent for the train set.

#### MODEL CONSTRUCTION AND TRAINING

In this work model was created with Python programming language and based on Keras package [34]. To get low prediction error and smooth plot, ANN was created with an increased number of weights and hidden layers, which were selected by experimenting and evaluated based on mean squared error. This study decided to use standard ReLU [35] activation function. Input layer has 3 parameters: temperature, ratio, pressure. After that model contains 4 hidden layers. First layer has 40 weights, second layer has 50, third hidden layer contains 30 and final 10. Output layer has only one parameter which is DNN model prediction of laminar burning velocity in meters per second. In order to compile model and get low errors, the RMSprop [36] was used as optimizer with changed learning rate. In this paper learning rate used for compilation is 0.0005. This made training of model take longer but more accurate. For model fitting batch size equal to 64 was selected. To make model fit well, 5 percent of train data was used for validation while the rest for training. Since RMSprop was used with low learning rate, ANN model works best with large number of epochs. For this paper 350 epochs were used. This way model did not overlearn and has low prediction errors.

#### **MODEL TESTING**

In machine learning model testing can be done couple of ways. One of the most popular and useful is cross-validation. However, cross-validation is best for classification tasks as it covers entire data part by part. For this paper testing was performed in a simpler way with similar idea as cross-validation has. It was done by performing 5 iterations. In other words, model was re-trained 5 times and tested on data it did not see yet. After each iteration data were mixed again and results written in the table. Doing this type of testing it is simple to cover large amount of data while simulating random data set for testing instead of made before validation. As Table 1 shows, in the end it is easy to calculate averages of every model evaluation criteria and also how trustworthy model can be. For comparison, MSE for train data is in interval 0.01-0.02, changes can be explained based on which part of data is used for predictions.

Test number	Mean Absolute Error (m/s)	Mean Squared Error (m/s) <sup>2</sup>	<b>R-Squared</b>
1	0.085	0.017	0.985
2	0.088	0.016	0.985
3	0.091	0.018	0.984
4	0.092	0.017	0.984
5	0.104	0.021	0.981
Average	0.092	0.018	0.984

Table 1. DNN model evaluation results

Moving to how model performed, Table 1 shows that average mean absolute error this model gets is equal to 0.092 m/s. These results are promising compared with mean absolute
errors from literature (0.3023 m/s) [6]. However, it is possible to reduce this error further by reducing experimental data spread rate as mean squared error is large for this data, however that depends on further experimental progress in the field. Yet, r-squared shows great results as its value is around 0.984 which means, that almost all used values were explained by the model.





Fig. 4. Pressure impact on LBV

Also, it is good idea to check if model keeps its form in entire field. As **Figure 3** shows, temperature changes still keep the smooth shape. In addition, raising temperature makes burning velocity bigger. Situation is inversed in Fig. 4, which shows pressure testing. Larger pressure makes velocity lower.

Final testing is to check how prediction graph with normal conditions matches experimental data. This will explain how model acts with areas which lack data for training.

From Fig. 5 it is clear that models predictions, which are marked by red line in the graph matches most of experiments from literature while ignoring remote data set points. With all those testing results, it is safe to say that model can deal with almost any data predictions in area marked earlier in this paper.



Fig. 5. ANN model prediction and experimental data comparison for normal conditions [6; 8-



Fig. 6. Model predictions (dots) compared with Malet correlation [37] (lines) at varied pressures and temperatures

It is known that experimental LBV data has higher uncertainty in the equivalence ratio interval 0.2-0.5 due to instabilities of lean hydrogen-air mixture flames [38]. For this reason in this range DNN model results were compared with Malet correlation [37], used for the prediction of LBV in the lean hydrogen-air mixtures. As can be noticed in Fig. 6, which presents comparison of LBV dependence on equivalence ratio at different pressures and temperatures, while the results of developed DNN model and correlation are very similar, Malet correlation shows less exponential LBV increase compared to the prediction by the developed DNN model. To test if DNN model is not showing worse prediction than Malet correlation, DNN results were compared with the experimental data [6; 8-32]. As Fig. 7 shows, while LBV values predicted by the developed DNN at equivalence ratios of 0.2 - 0.35 tend to correspond to the lower part of the available experimental spread, they are covered by the experimental data in this range.



Fig. 7. Model prediction and experimental data comparison in equivalence ratio interval 0.2-0.5 at normal conditions [6; 8-32]

# CONCLUSIONS

A DNN model predicting laminar burning velocities of hydrogen-air mixtures at different equivalence ratios, temperatures and pressures has been developed. Model was trained on about 2000 data points based on experimental and iterated data results. The model covers parameter region of 296-450 K temperature and 0.1-0.5 MPa pressure with average r-squared 0.984. Model works for dry mixtures only and up to equivalence ratio value of 5. The developed model is based on a more extensive experimental database than previous art found in literature. Also the approach to complimentary data simulation in current work is intended to be closer to the experimental values, to allow on-going non-complicated extension of the experimental database and relative weighting of different experimental results.

The model predictions were tested in relation to temperature and pressure variations and they show physically consistent results. More attention was given to the lean mixtures, were experimental uncertainties are higher. In this range model results were additionally compared to the prediction by Malet's correlation, often used to estimate LBV of lean hydrogen-air mixtures. Developed DNN model provided results similar to the correlation and covered by the experimental data.

Due to nonhomogeneity of experimental results it is expected for the model predictions to be less physically accurate in the parameter regions with fewer experimental data points or higher experimental errors. This could mean, that model still can lack training data in specific areas or that the data in these areas has a larger spread compared to the rest of training set. Therefore, even if this model showed good results it is possible to improve it by increasing database and forming it from more accurate experimental data in future.

The practical application of the developed model is planed in the future by incorporating trained model into the open-source turbulent premixed combustion solver flameFoam, developed at LEI.

Model material is available at

 $\underline{https://drive.google.com/drive/folders/1mkZyMLgsqXyJJg6lU8nAsLrp9XRHEW2s?usp=\underline{sharing}$ 

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# PROPERTY PREDICTION USING MACHINE LEARNING – A CASE STUDY OF METAL HYDRIDES

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#### ABSTRACT

Accurate prediction of reversible metal hydride formation enthalpy is one of the key requirements for a rapid design of new hydrogen storage and nickel-metal-hydride battery materials. In the last decades, DFT (density functional theory) approach showed good predictive potential for the ground state properties and accurate energies of hydride formation. However, calculating zero-point energy and temperature contributions in addition to 0K formation energy is computationally and time-consuming and therefore often avoided, hindering modelling of experimental behaviour.

Recently reported approach for universal machine learning in materials science based on a MatErials Graph Network (MEGNet), an implementation of DeepMind's graph networks, demonstrated very low prediction errors in a broad array of properties in both molecules and crystals, enabling hydride formation energy prediction with a DFT accuracy. In our work, we consider applications of this approach to the wide screening of potential dopants in reversible metal hydride materials, as well as the potential of transfer learning for the universal machine-learning model capable of addressing all contributions to hydrogen formation behaviour. Prediction of the formation energies for the Mg and Ni containing intermetallic hydrides, as well as the influence of various dopants, provides guide to the contribution of chemical nature and local structure to the destabilization of these hydrides.

Keywords: metal hydride, machine learning, DFT

# **INTRODUCTION**

In the pursuit of renewable energy solutions in the last decades, special attention is dedicated to the investigation and design of novel materials, which can serve in energy conversion or storage processes. Among those, metal hydrides continue to attract interest, given their wide use in hydrogen storage, thermal energy conversion [1] hydrogen compressors [2], and nickel-metal hydride batteries [3]. The importance of Mg and Ni in the materials for these applications was also determined by the data science approach of Rahnama and Sridhar [4]. Magnesium is seen as a potential candidate for stationary and mobile hydrogen storage, but the high stability of magnesium hydride limits its applications [5]. In order to meet requirements in regards to the stability of the hydride, i.e., achieve hydrogen desorption at low temperatures, alloying or doping with other elements is studied as a way of hydride destabilization or improvement of sorption kinetics [6]. In particular, complex Mg hydrides are widely studied [7]. Mg<sub>2</sub>NiH<sub>4</sub> complex hydride is seen as a compromise between hydrogen gravimetric density and hydride stability, where Ni acts to loosen the Mg-H bond. As opposed to the Mg<sub>2</sub>NiH<sub>4</sub>, which can be formed by hydrogen absorption in the intermetallic compound Mg<sub>2</sub>Ni, synthesis of Mg<sub>2</sub>FeH<sub>6</sub> must be achieved in other ways, since the starting binary alloy is not stable. Mg<sub>2</sub>FeH<sub>6</sub> forms a slightly more stable hydride than MgH<sub>2</sub> [8] which is of interest for thermochemical energy storage applications [9].

Regardless of the system in question, accurately predicting hydrogen formation/desorption enthalpy of some intermetallic compound, and also being able to determine the influence of various dopants on this property, has been a long-lasting goal of the research. Computational methods developed in the last century, especially the ones relying on the density functional theory (DFT), enabled accurate prediction of the electronic structure and stability of materials, providing tools for materials design which account not only the chemical nature (as seen in some empirical models) but also the crystal structure. In particular, predicting metal hydride enthalpies from the first principles within the error of 5-10 kJ/molH<sub>2</sub> is achievable for many metal hydride systems, given that the enthalpy changes in the hydride formation/decomposition reaction (at the temperatures close to the ambient one) can be reasonably approximated by the change in electronic energy calculated from the first principles [10] [11]. The contribution of the ZPE (zero-point energy) is not negligible, and must also be calculated in order to get the most accurate hydrogen absorption/desorption enthalpies [12].

Lately, development of the artificial neural networks (ANN) and machine learning (ML) applications in materials science promise new tools that can be trained on the large corpus of available DFT data to deliver predictions of properties of interest with high accuracy and much greater speed as compared to DFT calculations [13]. In our work, we demonstrate how DFT calculations can be complemented with a machine learning approach for a wide screening of suitable dopants for hydrogen storage applications of  $Mg_2NiH_4$  and  $Mg_2FeH_6$ .

# METHODOLOGY

#### **DFT calculations**

To model the effect of doping in Mg<sub>2</sub>NiH<sub>4</sub> and Mg<sub>2</sub>FeH<sub>6</sub>, band structure calculations of these hydrides, as well as intermetallic Mg<sub>2</sub>Ni, was done using a full potential (linearized) augmented plane-waves plus local orbitals (FP (L)APW + lo) method, as implemented in Wien2k program package [14] based on the density functional theory [15]. The exchange and correlation effects were included within the generalized gradient approximation, using the Perdew–Burke–Ernzerhof scheme. The radii of the muffin-tin non-overlapping spheres centered at the atomic nucleus were 2.0 bohr for Mg, 1.8 bohr for Fe and Ni, and 0.8 bohr for H. Mixed LAPW/APW+lo basis set was used, while the energy to separate core and valence states was -6Ry. The Brillouin zone integration was achieved via a tetrahedron method, using a mesh of 286 irreducible k-points for Mg<sub>2</sub>FeH<sub>6</sub> and 128 irreducible k-points for Mg<sub>2</sub>NiH<sub>4</sub>. Self-consistency was achieved by demanding that the convergence of the integrated charge difference within  $10^{-5}$ . The unit cell parameters were optimized, and the investigated structures were relaxed until the forces acting on all atoms were less than 1 mRy/bohr.

#### The methodology of machine-learning-based predictions

Starting from the fully optimized unit cells of  $Mg_2NiH_4$  and  $Mg_2FeH_6$ , models of doped hydrides were made, and dopants are selected among the 26 elements, mainly metals, of 4<sup>th</sup> or 5<sup>th</sup> period in Periodic system of elements (PSE). Substitution of Mg with other elements in Mg<sub>2</sub>NiH<sub>4</sub> was modelled by creating the supercell Mg<sub>7</sub>MNi<sub>4</sub>H<sub>16</sub>, where M represent substituting atoms listed in table 3. To model the substitution of iron by other metals, one of the four equivalent Fe atoms in the unit cell of Mg<sub>2</sub>FeH<sub>6</sub> was replaced with substituting atoms (M) listed in table 2, resulting in hydrides with supercell formula Mg<sub>8</sub>Fe<sub>3</sub>MH<sub>24</sub>. The unit cells of studied doped systems are shown in Fig.1. The resulting predictions for energies were scaled to the unit cells of formulas Mg<sub>2-x</sub>M<sub>x</sub>NiH<sub>4</sub> and Mg<sub>2</sub>Fe<sub>3/4</sub>M<sub>1/4</sub>H<sub>6</sub> where required.



Fig. 1. Unit cell of doped hydrides a) Mg<sub>7/8</sub>M<sub>1/8</sub>NiH<sub>4</sub> b) Mg<sub>2</sub>Fe<sub>3/4</sub>M<sub>1/4</sub>H<sub>6</sub>

For the prediction of the stability of the studied doped hydrides, a MatErials Graph Network (MEGNet) [16], an implementation of DeepMind's graph networks [17], was used. MEGNet demonstrated low prediction errors in a broad array of properties in both molecules and crystals, enabling hydride formation energy prediction with a DFT accuracy. Here mp-2019.4.1 model, trained on data set containing 133,420 data from the Materials Project [18], was used. Predicted energy of formation is in reference to the constituent elements in their standard state, and the mean absolute error (MAE) of predicted formation energies is 0.026 eV/atom compared to the DFT calculated values.

# **RESULTS AND DISSCUSSION**

# ML prediction of hydride formation energy

Prediction of the formation energy based on the graph made from the optimized structures is shown in Table 1 and compared to the DFT and experimental data. Formation energy for Mg<sub>2</sub>Ni is also calculated to determine hydride formation energy since this intermetallic compound is a starting point for the formation of  $Mg_2NiH_4$  (see equation 1, x=0).

Table 1. MEGNet prediction for the intermetallic stability ( $\Delta E^{ML}$ ) and hydrogen absorption energies ( $\Delta E_{hid}^{ML}$ ); comparison to DFT calculated values ( $\Delta E_{hid}^{DFT}$ ) and experimental values

$(\Delta \Pi_{\text{hid}}^{-1})$								
	$\Delta E^{ML}$	$\Delta E_{hid}{}^{ML}$	$\Delta E_{hid}^{DFT}$	$\Delta ZPE_{hid}$	$\Delta { m H_{hid}}^{ m exp}$			
	(eV/atom)	(kJ/molH <sub>2</sub> )	(kJ/molH <sub>2</sub> )	(kJ/molH <sub>2</sub> )	(kJ/molH <sub>2</sub> )			
Ma Fall	-0.3841	-110.8	-106.05 [19]	+14.6 [20]	-98 ± 3 [21]			
Mg <sub>2</sub> ren <sub>6</sub>			-93.4 [20]					
Mg <sub>2</sub> NiH <sub>4</sub>	-0.3140	-80.1	-81.0 [22]	+8.6 [23]	-64.0[24]			
Mg <sub>2</sub> Ni	-0.1795							

(ATT exp)

The proposed graph neural network (GNN) approach was shown to reproduce accurately DFT formation energies, for both intermetallic and hydrides. Therefore, based on the optimized structure of hydrides and, if needed, the optimized structure of the starting intermetallic alloy, obtaining hydride formation energy is straightforward, and agreement with the DFT results is good, as seen in Table 1.

However, this approach relies on the knowledge of reaction mechanisms. For example, a comparison of the  $\Delta E_{hid}^{ML}$  to the experimentally reported enthalpy for Mg<sub>2</sub>FeH<sub>6</sub> decomposition by Didisheim et al. [21] is very good, having in mind ZPE change in the reaction. However, other researchers report formation or decomposition of Mg<sub>2</sub>FeH<sub>6</sub> through the intermediate step of MgH<sub>2</sub> formation, and in such case much smaller experimental enthalpies have also been reported, i.e. -77 kJ/molH<sub>2</sub> [8].

Further, we consider the effect of doping of various elements (labelled M) in two cases: substitution of Fe with dopant in Mg<sub>2</sub>FeH<sub>6</sub>, and substitution of Mg with dopant in Mg<sub>2</sub>NiH<sub>4</sub>, as shown in Fig.1. Parameters were optimized using DFT calculations for the pure hydrides, Mg<sub>2</sub>NiH<sub>4</sub> and Mg<sub>2</sub>FeH<sub>6</sub>, starting from the experimental values and allowing volume change, lattice parameters ratio change (for Mg<sub>2</sub>NiH<sub>4</sub>), and relaxation of atomic forces. Basically, the structure with minimal energy is selected for a ground state. In such a structure, one of the Mg atoms is replaced with the M atom, where M is one of the elements from the 4th or 5th period of PSE. Details of the supercells used to model these compounds are presented in Table 2.

	space group no.	lattice parameter (Å)	cell angle (°)	atom site
Mg8Fe3MH24	221	a=b=c=6.437	α=β=γ=90.0	Mg (0.250 0.250 0.250) M (0.000 0.000 0.000) Fe (0.500 0.500 0.000) H (0.242 0.000 0.000) H (0.742 0.500 0.000) H (0.500 0.500 0.242)
	1	a=13.2516	α=90.0	Mg (0.671 0.435 0.030) Mg (0.329 0.065 0.506) Mg (0.000 0.000 0.000) Mg (0.500 0.500 0.036)
Mg7MNi4H16		b=14.4283	β=90.0	Mg (0.000 0.000 0.497) M (0.500 0.500 0.539) Ni (0.668 0.288 0.287) Ni (0.332 0.212 0.249) H (0.553 0.343 0.321)
		c=6.4419	γ=153.2	H (0.873 0.510 0.200) H (0.127 0.990 0.336) H (0.699 0.208 0.233) H (0.301 0.292 0.303) H (0.674 0.300 0.529) H (0.326 0.200 0.008)

Table 2. Details of the supercells used to model doping in the studied hydrides

The formation energy of M doped  $Mg_2FeH_6$  is equal to the predicted formation energy of the hydride, since it is calculated as:

$$\Delta E_{hid} = E(Mg_2Fe_{1-x}M_xH_6) - 2E(Mg) - (1-x)E(Fe) - xE(M) - 3E(H_2)$$
(1)

Table 3 summarizes the obtained results. Comparing to the hydride formation energy of the pure Mg<sub>2</sub>FeH<sub>6</sub>, -110.8 kJ/mol, we can see that most of the studied elements (all except Ti and Zr) as dopants lead to the destabilization of the hydride. This trend is in agreement with earlier DFT reports for Mn, Ni and Co-doped hydride [20], however, the amount of destabilization is largely underestimated as compared to DFT. For example, Co doping was found to decrease hydride formation energy by 12.6 kJ/molH<sub>2</sub> [20], while only a 2.8 kJ/molH<sub>2</sub> decrease is seen in ML predicted energies.

м	$\Delta E^{ML}$	$\Delta E_{hid}^{ML}$
IVI	eV/atom	kJ/molH <sub>2</sub>
Li	-0.3354	-97.1
Be	-0.3534	-102.3
Na	-0.3094	-89.6
Mg	-0.3430	-99.28
Al	-0.3505	-101.4
K	-0.2708	-78.4
Ca	-0.3359	-97.2
Sc	-0.3725	-107.8
Ti	-0.3861	-111.7
V	-0.3785	-109.6
Cr	-0.3703	-107.2
Mn	-0.3782	-109.4
Со	-0.3732	-108.0
Ni	-0.3505	-101.3
Cu	-0.3257	-94.3
Zn	-0.3235	-93.6
Ga	-0.3284	-95.1
Sr	-0.3264	-94.5
Y	-0.3617	-104.7
Zr	-0.4009	-116.0
Nb	-0.3751	-108.6
Мо	-0.3881	-112.3
Ru	-0.3804	-110.1
Rh	-0.3758	-108.8
Pd	-0.3744	-108.4
Ag	-0.3200	-92.6
In	-0.3323	-96.2

Table 3. MEGNet prediction of formation energy of  $Mg_2Fe_{1-x}M_xH_{6}$ ,  $\Delta E_{hid}^{ML}$ 

Further, we discuss the substitution of Mg in reversible hydride,  $Mg_2NiH_4$ . Hydride is formed by hydrogen absorption in  $Mg_2Ni$ , and hydride formation energy of doped hydride is calculated as:

$$\Delta E_{hid} = E(Mg_{2-x}M_xNiH_4) - E(Mg_{2-x}M_xNi) - 2E(H_2).$$
<sup>(2)</sup>

Since formation energy prediction is in reference to the elements in their standard state, equation 2 becomes:

$$\Delta E_{hid}^{ML} = \Delta E^{ML} (Mg_{2-x}M_xNiH_4) - \Delta E^{ML} (Mg_{2-x}M_xNi).$$
(3)

The results are presented in Table 4. Comparison of the results to the DFT work shows excellent agreement for the Co and Cu doping: DFT calculated formation energy of - 66.6kJ/molH<sub>2</sub> and -65.6 kJ/molH<sub>2</sub> for Co and Cu doped Mg<sub>2</sub>NiH<sub>4</sub> respectively, is reported [25]. However, one should have in mind that Mg is immiscible with V, Cr, and Fe, and therefore any ternary phases tend to decompose into more stable binary intermetallics upon cycling. Therefore, the approach we used for the prediction of hydride formation energy might lead to overestimation of the doped hydride stability in some cases.

м	$\Delta E^{ML}(Mg_{2-x}M_xNiH_4)$	$\Delta E^{ML}(Mg_{2-x}M_xNi)$	$\Delta E_{hid}{}^{ML}$
IVI	eV/atom	eV/atom	kJ/molH2
Li	-0.3273	-0.1673	-86.3173
Be	-0.2240	-0.1275	-57.1927
Na	-0.3222	-0.1007	-94.234
Al	-0.2691	-0.2200	-59.0356
K	-0.2787	+0.0101	-95.58
Ca	-0.3395	-0.1096	-98.7882
Sc	-0.3705	-0.2572	-87.8948
Ti	-0.3461	-0.1908	-89.2649
V	-0.3114	-0.1321	-86.0423
Cr	-0.2947	-0.1046	-84.3827
Mn	-0.3002	-0.1198	-84.0402
Fe	-0.2699	-0.0852	-78.8154
Со	-0.2581	-0.1161	-70.3583
Cu	-0.2667	-0.1589	-67.0681
Zn	-0.2658	-0.1935	-61.7565
Ga	-0.2533	-0.2151	-54.409
Sr	-0.2999	-0.0370	-95.9226
Y	-0.3707	-0.2084	-95.0252
Zr	-0.3686	-0.2167	-93.1148
Nb	-0.3268	-0.1485	-88.8694
Мо	-0.2894	-0.0819	-85.8783
Ru	-0.2598	-0.1446	-66.8076
Rh	-0.2845	-0.2263	-63.3244
Pd	-0.2901	-0.2350	-63.9564
Ag	-0.2638	-0.1675	-64.8441
In	-0.2674	-0.2010	-61.2114

Table 4. MEGNet prediction of formation energy ( $\Delta E^{ML}$ ) of  $Mg_{2-x}M_xNiH_4$  and  $Mg_{2-x}M_xNi$ , and predicted hydride formation energy  $\Delta E_{hid}^{ML}$ 

Figures 2 and 3 visualize the dopant effect in the studied cases, for the dopants belonging to the  $4^{th}$  and  $5^{th}$  periods.



Fig. 2. Plot of the doping effect of 4<sup>th</sup> period elements on hydride formation energy for b) Mg<sub>2</sub>Fe<sub>3/4</sub>M<sub>1/4</sub>H<sub>6</sub> (orange, left) and Mg<sub>7/8</sub>M<sub>1/8</sub>NiH<sub>4</sub> (purple, right)



Fig. 3. Plot of the doping effect of 5<sup>th</sup> period elements on hydride formation energy for b) Mg<sub>2</sub>Fe<sub>3/4</sub>M<sub>1/4</sub>H<sub>6</sub> (orange, left) and Mg<sub>7/8</sub>M<sub>1/8</sub>NiH<sub>4</sub> (purple, right)

Comparing the influence of dopants in  $Mg_2FeH_6$  and  $Mg_2NiH_4$ , we can conclude that due to the local structure and nature of the element being replaced (Mg or Fe) qualitatively different behaviour is seen, for both 4<sup>th</sup> and 5<sup>th</sup>-period elements as dopants. Choice of the substitution element in Mg<sub>2</sub>NiH<sub>4</sub> can be made such to either destabilize or stabilize hydride and in general we see that elements from the left part of the period cause increase in the stability of the hydride, while larges destabilization is seen for the elements at the right end of the period. The main reason of such phenomena could be in the strength of the bond that such of the elements make with hydrogen – this trend resembles stability of binary hydrides, which decrease down the period. For the substitution of Fe in Mg<sub>2</sub>FeH<sub>6</sub>, we can see that the larger the discrepancy of iron and dopant element electronic structure, the larger destabilization can be expected. However, given the coordination of 6 hydrogen atoms around Fe is related to the iron electronic structure, a change of the coordination in the doped hydrides is also expected. Looking at Figs. 2 and 3, we can also conclude that the graph approach of the used model is suitable for addressing the influence of both chemical nature and local structure. Reservation in regard to these results is related to the absence of relaxation of the doped structures, and significant quantitative difference between DFT calculated and ML predicted formation energies for the Mg<sub>2</sub>FeH<sub>6</sub> doped systems. Therefore, further steps in machine learning for the structure optimization as well as the optimization of the GNN model would ensure the most accurate predictions of hydride formation enthalpies.

# Discussion of the potential of transfer learning to the prediction of hydride formation enthalpy

In order to make a highly accurate prediction of the experimental values of hydride formation enthalpy, besides the prediction of DFT electronic energy, the contribution of ZPE should also be added. MEGNet models are trained to predict ZPE for molecules; however, these computations are very demanding for crystals, and results are reported for a small number of compounds. Instead of training on the calculated ZPE data, we considered training a model on experimental data available in the DOE SNL database [26] and listed in literature [12]. This corpus of experimental data related to the reversible metal hydrides is intersected with the Materials project database [18] to obtain structures and energies of the starting metal/alloy and corresponding hydride, and form a graph representation input of the hydride. However, this

search is limited only to the cases where a single, known, crystal structure of the alloy and hydride phase occurs, and this is not so often the case in experimental work. Therefore, only 34 hydrides were found, and the experimental enthalpy and DFT calculated hydride formation energy is presented in Fig. 4.



Fig. 4. Comparison of the literature values of hydride formation enthalpy and DFT calculated hydride formation energy from Materials project data [18]

On this dataset, we tried to apply transfer learning, relying on the embeddings obtained in the MEGNet model, to account for ZPE and other reasons for discrepancies. However, this dataset was shown to be too small for such a task, and overfitting during training could not be avoided, given that calculation of property such as ZPE requires a complex architecture of the ANN. An additional problem comes from the fact that ANN should also be trained to predict the most stable structure of the staring intermetallic compound (for example, in here studied case, to know that  $Mg_2FeH_6$  will be formed directly from elements, while  $Mg_2NiH_4$  will be formed starting from the stable  $Mg_2Ni$  intermetallic compound). Therefore, future work is expected to solve these problems and address adaptation of GNN for the complex problematics of hydride formation.

# CONCLUSION

In this work, we consider the application of machine learning to the prediction of hydride formation energy. MEGNet model is used to predict the stability of Mg<sub>2</sub>NiH<sub>4</sub>, Mg<sub>2</sub>Ni, and Mg<sub>2</sub>FeH<sub>6</sub>, as well as the hydride formation energy of Mg<sub>2-x</sub>M<sub>x</sub>NiH<sub>4</sub> and Mg<sub>2</sub>Fe<sub>1-x</sub>M<sub>x</sub>H<sub>6</sub>, where M is one of 26 elements, mainly metals. Good agreement with DFT results is seen for Mg<sub>2-x</sub>M<sub>x</sub>NiH<sub>4</sub> doped hydrides, while for Mg<sub>2</sub>Fe<sub>1-x</sub>M<sub>x</sub>H<sub>6</sub> trend is predicted but the dopant effect is underestimated. Comparing the influence of dopants in Mg<sub>2</sub>FeH<sub>6</sub> and Mg<sub>2</sub>NiH<sub>4</sub>, we show how hydride formation energy can be tuned, and how, due to the local structure and nature of the element being replaced same dopants have different influence. Choice of the substitution element in Mg<sub>2</sub>NiH<sub>4</sub> can be made such to either destabilize or stabilize hydride and in general we see that elements from the left part of the period cause increase in the stability of the hydride, while larges destabilization is seen for the elements at the right end of the period.

In order to predict experimental values with high accuracy, additional factors in addition to formation energy must be taken into account. In particular, temperature effect should be considered, and ZPE contribution should be added, given that vibrations of a light elements (such as Li or Mg) as well as hydrogen atom are not negligible in the hydrides. We propose that this can be done by using transfer learning and MEGNet embeddings in combination with experimental data. We demonstrate good accuracy for the fast screening of potential dopants, and further steps in the application of this approach are related to the improvement of the model for the doped systems, as well as pre-step of machine learning relaxation of the doped structures prior to the prediction of hydride formation enthalpy.

# ACKNOWLEDGEMENT

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# DESIGNING OF A HIGH-PRESSURE TANK FOR HYDROGEN STORAGE

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#### ABSTRACT

Hydrogen which is the most abundant element in nature is also an energy transmitter and seen as the energy source of the future. However, the storage which is the common and significant problem of the energy systems is also valid for the hydrogen. Technologies concerning the storage of hydrogen are evolving. Especially with the development of technologies of materials, the variable and innovative solutions have been found for the storage of this energy source. In this study, the subject is focused on the storage of hydrogen in the gas state. Firstly, geometric calculations of type III high-pressure hydrogen tank with a design pressure of 70 MPa were made with the help of geometric equations which were formulated according to the ideal gas law and vessel geometry. Then, the thickness of the storage vessel calculated by the choice of the metal liner as aluminum and the composite material as carbon fiber. The thickness of the storage vessel determined according to standards, acceptances and the safety factor. After the theoretical calculation of the design criteria, the mechanical analyses were performed and the safety and reliability of the designed tank were tested. The storage tank had its mechanical analyses, prioritizing Von-Mises Equivalent Stress Analysis, is carried out using the program ANSYS, in this manner the safety and insurance of the designed storage tank are tested on the digital environment and successfully concluded.

**Keywords**: Storage of Hydrogen, High-Pressure Gas Hydrogen Storage Tank, Type-3 Storage Tank, ANSYS Mechanical Analysis

#### INTRODUCTION

The first chemical element of the periodic table, hydrogen, can be regarded as the primary energy source of the universe. Today, interest in hydrogen energy, which is one of the alternative sources of energy, is rapidly increasing. Storage methods for the viable use of hydrogen energy are of great importance. With the effective storage of hydrogen, the solution for the major problem of energy systems, which is storage, will be offered [1].

Hydrogen can be stored dissolved in metals in a solid, in cryogenic vessels in liquid phase or high-pressure tanks in the gas. The method of the storage of hydrogen in the gas state is still the most simple, common and efficient technologies in use. High-pressure storage tanks can be produced in four types according to the materials and methods used. Type 1 vessels constructed from steel and aluminum alloys, Type 2 vessels constructed from glass fiber/aramid material wrapped around the metal liner, Type 3 vessels constructed from composite material both axially and ring-shaped wrapped around the metal liner, and Type 4 vessels constructed from composite material both axially and ring-shaped wrapped around the polymer liner [2].

Han and Chang [3] carried out studies on the modelling of TYPE III hydrogen tanks, application of strength equations and adaptation of designed tanks for vehicle use. Macuzzo et al. [4] designed and performed a static analysis of the hydrogen tank which has combined solid-

phase storage that dissolved in metal and high-pressure gas-phase storage. Cumalioglu [5] developed a high-pressure storage tank design with a dynamic wall, which is a new method in the design of hydrogen storage tanks in the gas phase. Also carried out static analyses in the ANSYS program of the designed storage tank. Hua et al. [6] compared the TYPE III and TYPE IV tanks in their study, both in terms of performance and cost and gave detailed information about the feasibility of high-pressure hydrogen storage tanks with the reports and figures they made. Kamel et al. [7] carried out studies on the use of composite materials in high-pressure hydrogen storage tanks and developed equations which would provide the modelling of the tank and the strength calculations.

In this study, firstly geometric calculations of TYPE III high-pressure hydrogen tank with a design pressure of 70 MPa were made with the help of geometric equations that were extracted according to the ideal gas law and vessel geometry. Then, the thickness of the storage vessel calculated by the choice of the metal liner as aluminum and the composite material as carbon fiber and the thickness of the storage vessel was determined according to standards, assumptions and the safety factor. The designed high-pressure hydrogen tank was also concluded by static analysis carried out in the ANSYS program. The calculations and static analysis are made neglecting the position of the valve.

# METHODOLOGY

#### **Design of a Storage Tank**

Depending on the area and sector to be used, a wide variety of vessels can be designed and produced, but a vessel can be produced more efficiently for its intended use according to its specific design for the specified values, conditions and materials. First of all, the design criteria of the vessel should be calculated with the help of mathematical equations. For this, the internal volume of the vessel is found at first from the gas equations. Then the calculations of the diameter and length are made according to the appropriate standards. Concerning design pressure and material yield strength, wall thicknesses are also found. These values can be revised again according to the results of analyzes and tests.

Under normal circumstances, hydrogen gas is considered as an ideal gas and calculations can be made according to these assumptions. However, as in the scope of this study, when very high pressures such as 50, 70 MPa are reached, it is far from being an ideal gas. Therefore, to be able to make a healthy and coherent calculation, the compressibility factor symbolized by "z" must be known. Table 1 shows the values of the compressibility factor "z" according to various pressures. Using this table compressibility factor is taken as z = 1.4554 for the tank design pressure of 70 MPa.

P (MPa)	10	20	30	40	50	60	70	80	90
Z	1.0601	1.1244	1.1904	1.2569	1.3233	1.3895	1.4554	01.5209	1.5858

Table 1. Table of the compressibility factor/pressure of the hydrogen [5]	5]	]
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The following equation is used to find the specific volume value. R = 4124 J / kg.K is found by thermodynamic tables.  $T = 0 \circ C = 273.15 \text{ K}$ , the assumption of temperature is made under normal circumstances. As a result of the equation (1), the specific volume was calculated as  $v = 0.023422 \text{ m}^3/\text{kg.}$   $P \times v = z \times R \times T \quad ^{(1)}$ 

The internal volume of the tank can be calculated using the following equation. The weight of the hydrogen tank is assumed as 10 kg, as the specified design criteria. As a result of the equation (2), the internal volume of the tank was calculated as 0.23422 m<sup>3</sup>.

$$V = v \times m \quad ^{(2)}$$

The geometry of the tank is arranged to have semi-spherical headers on and below a cylindrical shape. As a result of the literature search especially by reference to the ASME American Society of Mechanical Engineers) standards [8], it was deemed feasible to take the length/diameter ratio (L / D) as 3 in the optimal form. The radius (r) and length (L) values used to determine the tank dimensions can be calculated using the following equation (3). The result of the equation is calculated as r = 0.241 m and as a result L = 3D = 1.445 m.

(3)

$$V = \left(2 \times \frac{4}{3} \times \frac{1}{2} \times \pi \times r^3\right) + \left(\pi \times r^2 \times (L - 2r)\right).$$

Material selection is very important in high-pressure tank design. The tank to be designed will be of TYPE3 high-pressure tank. TYPE3 tanks are characterized by the fact that they can be stored at very high pressures by integrating with the composite layer around the metal liner to increase the tank strength. The selection of metal and composite materials must be done for the production of the tank. In this study as the metal material, aluminum, which is cheap and frequently used in industry and as the composite material, carbon fiber which is durable enough to withstand a very high pressure of 70 MPa, is quite light and thus makes the storage tank easy to use, are selected. The thickness of the layers to be formed can be calculated using the following equation after the material selection and determination of the material properties.

$$t = \frac{P \times D \times SF}{YS} \quad ^{(4)}$$

The thickness of the carbon fiber layer was found to be 29.7706 mm. However, in terms of both production and design ease, this value can be updated to 30 mm. In this condition, the safety factor of the tank is increased and a more stable and reliable high-pressure storage tank design was made. And the aluminum layer is determined as 10 mm according to ASME standards. The reason for the aluminum layer to be 10 mm is to ensure the stability and impermeability of the tank without increasing the total cost. Table 2 shows the design criteria of the high-pressure hydrogen storage tank.

PROPERTIES	VALUES
Operating pressure	70 MPa
Hydrogen capacity	10 kg
Diameter	562  mm = 0.56  m
Length	1526 mm = 1.53 m
Length/diameter ratio	3.0
Internal volume	$0.23422 \text{ m}^3 = 234.22 \text{ L}$
Metal liner material	EN AW / Al99Cu / 1100 / O Aluminum, Yield Strength of 28 MPa
Composite layer material	TORAYCA T700S Carbon Fiber, Yield Strength of 2550 MPa
Metal liner thickness	10 mm
Composite layer thickness	30 mm

Table 2. Design criteria of the high-pressure hydrogen storage tank.

Storage tank type	TYPE III
Header angle	45°
Safety factor	2.25

Figure 1 shows the two-dimensional mechanical drawing and three-dimensional representative image of the storage tank.



Fig. 1. Two-dimensional mechanical drawing (a) three-dimensional representative image (b) of the storage tank

#### Static Analysis of the Storage Tank

After the theoretical calculation of the design criteria, the static analysis was performed and the safety and reliability of the designed tank were tested. One of the most commonly used programs in static analysis is ANSYS which is a computer-aided engineering program and provides analysis and simulations in engineering studies. Analysis of objects in complex structures can be done with ANSYS Mechanical. The real-world behaviour of these subsystems is simulated in this program which is using the finite element method and realistic results are obtained. The static analysis of the designed storage tank within the scope of the study has been done in the R19.2 Academical version of the ANSYS program.

After the geometry of the storage tank is drawn, the first step is to assign the material information. Carbon fiber (dark blue, outer part) and aluminum (gray, inner part) materials are defined as shown in Fig. 2. The storage tank was subjected to the fixation process in the program in adterms of real-world behaviour.



Fig. 2. Materials of the storage tank

The second step in the static analysis is the mesh generation. Mesh generation can be defined as the process of splitting a physical definition range into smaller definition ranges (elements). The purpose here is to facilitate the solution of a differential equation. Therefore, the approximate accuracy of the results to be obtained in the finite element method depends on the type of element used and the number of elements used on the geometry. Figure 3 shows the mesh generation made to the storage tank.

The next step is to define the design pressure value and the application area. The design pressure value 70 MPa is defined in the program to the inner surface of the storage tank, as shown in Figure 4.





Fig. 3. The mesh structure

Fig.4. Design pressure and vector

#### **RESULTS AND DISCUSSION**

Von-Mises equivalent stress analysis is the most important analysis result regarding the feasibility of the storage tank. As a result of this analysis, the value and the position of the maximum stress in the storage tank will be learned. Figure 5 shows the results of the analysis of the storage tank from various profiles and angles. As seen from the legend situated on the left side of the figure, the lowest equivalent stress value in the storage tank according to the Von-Mises equivalent stress analysis is 41.311 MPa and the maximum equivalent stress value is 1125.4 MPa.

Carbon fiber material with a yield strength of 2550 MPa was selected in the storage tank design. Therefore, the storage tank designed to withstand an operating pressure of 70 MPa, since the equivalent stress of 1125.4 MPa is smaller than the yield strength of the selected material. Also, the difference between these stress values is as high as the safety factor multiplier. As a result, it is understood from the analysis that the designed storage tank is safe and reliable.



Fig. 5. The predicted Von-Mises equivalent stresses in different views

The deformation analysis is carried out to measure, determine and analyse the positional changes which can occur in the storage tank. The deformation test is significantly important to detect an existing problem or to predict possible problems. As seen from Figure 6, the deformation of the designed storage tank is at most 4.4022 mm.

To measure the applied force gradually and to measure the amount of elongation in the sample, equivalent elastic strain analysis has been performed to the designed storage tank. As shown in Figure 7, this result shows that a maximum of 0.016981 mm of strain will occur at every 1 mm. This ratio, which is slightly more than 1%, can be tolerated and does not impair the safety of the tank.



Fig. 6. The predicted total deformation



Fig. 7. The predicted equivalent elastic strain

In the analysis of the safety factor to the designed storage tank, it is seen in Figure 8 that the aluminum layer is challenging on the value of 0.02488. On the contrary, the safety factor in the carbon fiber layer reaches up to 15. The importance of composite materials such as carbon fiber in high-pressure tanks is thus proven.



Fig. 8. The predicted safety factor

# **CONCLUDING REMARKS**

In this study, Type III high-pressure hydrogen storage tank is designed and analyzed by the finite element method in the ANSYS program. In the first step, the internal volume of the tank was calculated from the ideal gas law as the specific volume and then the internal volume was found for 10 kg as the design capacity. The geometry of the storage tank was subjected to volume calculations under the assumptions of the headers being half-spherical at 45  $^{\circ}$  angle, the main part being cylindrical, and the ratio between the diameter of the storage tank and the length of the storage tank, which is considered to be 3. By the calculations made with the yield strength values of carbon fiber and aluminum selected, the wall thicknesses of these two layers were determined and the high-pressure hydrogen tank design was completed.

The analyses carried out in the ANSYS program gave the necessary results of this study. The thermal stress during the filling and emptying the tank assumed being in the safe limit if the static analyses resulted in safe parameters. In the static analysis according to the Von Mises Equivalent Stress Criteria, the maximum equivalent stress value to be formed in the storage tank is 1125.4 MPa, and the selected carbon fiber material has a yield strength of 2550 MPa, indicating that the designed storage tank is just as safe as the safety factor of 2.25. As a result, in this study,  $1526 \times 562$  mm size, 10 mm aluminum and 30 mm carbon fiber layer thickness, half-spherical cylindrical high-pressure hydrogen storage tank which has a capacity of 10 kg of hydrogen at an operating pressure of 70 MPa is very safe and reliable as seen in the analyses.

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# HYDROGEN DIFFUSION AND TRAPPING IN DISTINCT MICROSTRUCTURES OF 42CRM04 STEEL

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#### ABSTRACT

The expanding utilization of hydrogen in contact with medium and high-strength structural steels has increased the number of investigations carried out to study the impact of hydrogen on their mechanical properties. Nowadays, it is well known that the presence of hydrogen decreases the mechanical properties of ferritic steels, giving rise to the phenomenon known as hydrogen embrittlement (HE). The sensitivity to HE increases with the strength of the steel due to the increase of its microstructural defects (hydrogen traps), that eventually increase hydrogen solubility and decrease hydrogen diffusivity in the steel. In this context, the aim of this work was to study hydrogen diffusivity in a 42CrMo4 steel heat treated to obtain quite different microstructures, with a broad range of hardness levels because 42CrMo4 steel is widely used for the manufacturing of pressure vessel for the storage and transport hydrogen. Electrochemical hydrogen permeation tests were performed in a modified Devanathan and Stachursky double-cell, allowing the determination of the apparent and lattice hydrogen diffusion coefficients. In addition, scanning electron microscopy (SEM) was used to examine the steel's microstructures in order to understand their interaction with hydrogen atoms. In general, the results show that the permeation parameters are directly related to the steel hardness, being barely affected by the steel microstructure.

**Keywords:** Hydrogen embrittlement, 42CrMo4 steel, heat treatments, hydrogen diffusion, hydrogen permeation tests.

#### **INTRODUCTION**

In a global context of environmental awareness, the utilization of hydrogen as an energy source has been studied in recent years [1,2]. Due to its versatility and zero  $CO_2$  emissions, hydrogen is supposed to be a good choice for future energy systems. Therefore, the study of new materials that can store and transport hydrogen has become a topic of general interest [3]. Specifically, medium and high-strength steels have been used in numerous investigations in order to know the influence of hydrogen on their mechanical properties [4,5].

On the other hand, hydrogen can be absorbed by steel during fabrication (electroplating, electrochemical machining, pickling, welding, etc.) and during its service (cathodic protection of offshore structures, pipes and vessels, etc.) giving rise to the hydrogen embrittlement (HE) phenomenon [6]. A large number of structural failures have occurred due to HE. These failures take place under stress levels lower than the design stress, are brittle in appearance and sometimes very difficult to predict. Consequently, steel structures that work in the presence of hydrogen must be designed with steels capable of withstanding its embrittlement effect, bearing in mind that the deterioration of mechanical properties (loss in ductility, reduction of fracture toughness, reduction in strength and crack growth rate enhancement) is known to increase with the strength of the steel [4, 7].

Hydrogen disffusion and trapping in steels have been studied in order to describe the HE process. Hydrogen atoms have a high mobility in BCC steel lattices, which implies that can easily interact with their structural defects, where they can be temporarily or permanently

trapped. It is known that hydrogen atoms can be retained in steel's traps such as vacancies, dislocations, grain boundaries, matrix-carbides interfaces and other internal interfaces [8]. These traps can be classified as reversible and irreversible depending on their ability to retain hydrogen at room temperature. Irreversible traps have a high trap activation energy, therefore the hydrogen trapped in them behaves as non-diffusible. In contrast, sites with lower trap activation energy constitute reversible traps, which simply delay hydrogen diffusion [9].

Among all the available techniques to study the hydrogen diffusion and trapping phenomena in steels, electrochemical hydrogen permeation has proven to be one of the most reliable methods [10,11]. For instance, Parvathavarthini et al. [12] studied hydrogen diffusion and trapping in a 2.25Cr1Mo steel submitted to a variety of heat treatments, reporting an inverse correlation between steel hardness and hydrogen diffusivity. This is in line with the findings of other authors, such as Depover et al. [13]. They agree that the dislocation density reduction that takes place during certain heat treatments are responsible of decreasing the density of hydrogen traps and thus increasing hydrogen diffusivity. Regarding the 42CrMo4 steel used in this study, Zafra et al. [14] already assessed the influence of the tempering temperature in the hydrogen permeation parameters, but some other aspects, such as the influence of the tempering time in these treatments and the influence of the austenitization temperature in normalizing and annealing treatments still need to be thoroughly examined.

Consequently, electrochemical hydrogen permeation tests have been performed in this study in order to study hydrogen diffusivity in a 42CrMo4 steel submitted to different heat treatments. Different microstructures were produced by means of different annealing, normalizing and quench and tempering treatments. The influence of the austenitization temperature and the tempering time was analysed.

#### **EXPERIMENTAL PROCEDURE**

#### **Steel and heat treatments**

The material studied in this work was a 42CrMo4 steel (0.42%C-0.98%Cr-0.22%Mo-0.62%Mn-0.18%Si). In order to analyse the influence of the steel microstructure on its hydrogen permeation behaviour, different heat treatments were carried out onto hot rolled plates (250 x 125 x 12 mm). The obtained steel grades and their correspondent heat treatments are shown in Table 1.

Steel grade	Heat treatment				
QT600-3min	845°C/40min + water quenched + 600°C/3min tempering				
QT600-30min	845°C/40min + water quenched + 600°C/ 30min tempering				
QT600-2h	845°C/40min + water quenched + 600°C/2h tempering				
QT600-24h	845°C/40min + water quenched + 600°C/24h tempering				
QT600-7d	845°C/40min + water quenched + 600°C/7d tempering				
QT725-4h	845°C/40min + water quenched + 725°C/4h tempering				
845FC	845°C/40min + furnace cooled				
1050FC	1050°C/40min + furnace cooled				
845AC	845°C/40min + air cooled				
1050AC	1050°C/40min + air cooled				

Table 1 - Heat treatments applied to 42CrMo4 steel and obtained steel grades

#### Hardness and microstructural characterization

For the microstructural characterization, the specimens were firstly ground with SiC papers of different grit (60 to 1200) and then polished in synthetic cloths with 6  $\mu$ m and 1 $\mu$ m diamond pastes. After completing the polishing process, samples were etched with Nital-2% and their microstructures observed using a JEOL-JSM5600 scanning electron microscope (SEM). In addition, Vickers hardness measurements were performed applying a load of 31 kg for 15 s.

# Hydrogen permeation tests

Hydrogen permeation tests were performed on all the steel grades shown in Table 2 in order to determine the hydrogen diffusion and trapping behaviour. Before testing, specimens of  $30 \times 25$  mm with a thickness of between 0.7 and 1 mm, depending on the steel grade, were ground and then polished, as already mentioned. Specimens were finally cleaned with water and then with acetone prior to starting the test.

The permeation tests were carried out in a double electrolytic cell based on the one developed by Devanathan and Stachurski [15], as it is shown in Fig.1.



Fig. 1. Modified D-S double-cell employed in the hydrogen permeation experiments

Hydrogen generation occurs in the cathodic cell, which was filled with 300 ml of an acid solution (pH  $\approx$  1) composed of 1M H<sub>2</sub>SO<sub>4</sub> and 0,25 g/l As<sub>2</sub>O<sub>3</sub>. In this case, H<sub>2</sub>SO<sub>4</sub> is the hydrogen donor and As<sub>2</sub>O<sub>3</sub> is added to limit the hydrogen recombination reaction [11]. The anodic cell, where hydrogen oxidation occurs, was filled with 300 ml of a basic solution (pH $\approx$ 12) of 0.1 M NaOH. Both cells meet the ASTM G148 recommendation of a solution volume-to-surface area ratio greater than 20 ml/cm<sup>2</sup> [18]. The cells are separated by the specimen, which is the working electrode (WE) in each cell. A circular exposed area of 1.25 cm<sup>2</sup> was always used. In addition, to ensure that only hydrogen oxidation is taking place in the anodic cell and to assure the oxidation of all hydrogen atoms, a thin palladium coating is applied in the specimen's anodic surface. This coating was electrochemically deposited from a palladium solution of 2 g/l of Pd, applying a current density of 3mA/cm<sup>2</sup> for 5 min.

Thin platinum plates with a total surface area of 1 cm<sup>2</sup> were used as counter electrodes (CE) in each cell. In the anodic cell a reference silver/silver chloride electrode (Ag/AgCl, RE)

was also employed. Finally, for data acquisition, a pocketSTAT Ivium potentiostat was used. A value under 0.1  $\mu$ A/cm<sup>2</sup> in the background current measured in the anodic cell is needed before starting the tests. All tests were run at room temperature.

The permeation method employed in this study consisted in recording several partial build-up permeation transients by sequentially increasing the applied cathodic current density until reaching a steady-value of the hydrogen diffusion coefficient. Thus, plotting the recorded permeation current density,  $J_p$  (in  $\mu A/cm^2$ ), versus time, a representation as shown in Fig. 2(a) is obtained. In the end, the saturation of all microstructural traps is reached at the last transients, where the value of the lattice hydrogen diffusion coefficient,  $D_L$ , can be obtained [14]



Fig. 2. (a) Characteristic build-up permeation transients produced increasing the cathodic current density  $(0.5 + 0.5 + 1 + 1 + 1 + 1 \text{ mA/cm}^2)$  and (b) example of D<sub>app</sub> calculation

The cathodic current density was increased in steps of 0.5 mA/cm<sup>2</sup>, for the first two transients, and of 1 mA/cm<sup>2</sup> for the further ones. The apparent hydrogen diffusion coefficient ( $D_{app}$ ) was calculated at each transient following the time lag ( $t_{lag}$ ) method described in the ASTM G148 standard [19]. Equation (2) was used for  $D_{app}$  determination:

$$D_{app} = \frac{L^2}{M \cdot t_{lag}},\tag{2}$$

where L is the specimen thickness, M a constant with a value of 6 (for  $J = 0.63J_{ss}$ ), and  $t_{lag}$  is the time needed to reach the 63% of the steady-state permeation current state,  $J_{ss}$  (see Fig. 2(b)).

#### RESULTS

#### Microstructural characterization

#### Quenched and tempered 42CrMo4 steel

The SEM microstructures of the six quenched and tempered 42CrMo steel grades, are shown in Fig. 3 under a magnification of 5000x. In addition, the average Vickers hardness, HV30, measured on each steel grade is given in Table 2.



Fig. 3. SEM micrographs (5000x) of Q+T 42CrMo4 steel grades. (a) QT600-3min, (b) QT600-30min, (c) QT600-2h, (d) QT600-24h, (e) QT600-7d and(f) QT725-4h

The microstructure of all these 42CrMo4 steel grades was tempered martensite except for QT600-3 min steel grade (Fig. 3(a)), in which, due to the extremely short duration of the tempering treatment, it was basically untempered martensite, with a hardness of 484 HV30. For the rest of the treatments, it is noted that the tempering time is inversely related to the microstructure acicularity and thus the distortion of the martensitic structure (dislocation density) [17]. It is also worth noting that carbide size and morphology is strongly related to the tempering time. In fact, the elongated carbides precipitated first along grain and martensitic lath/pack/block boundaries, as can be observed in the least tempered steel grades, such as QT600-30 min, but then carbides break up, grow, globulize, and distribute more homogeneously as the tempering time increases. According to these microstructural changes, the hardness of the steel decreases considerably with the tempering duration, as it was recorded in Table 2.

Furthermore, the greatest effect of tempering was produced in the steel grade tempered at 725°C for 4h, as observed in Fig. 3(f). Dislocation density and internal stress levels are also supposed to be the lowest of all the Q+T steel grades as it presents the lowest hardness, 206 HV30.

Steel grade	Microstructure	Hardness, HV30
QT600-3min	Untempered martensite	484
QT600-30min	Tempered martensite	333
QT600-2h	Tempered martensite	307
QT600-24h	Tempered martensite	280
QT600-7d	Tempered martensite	244
QT725-4h	Tempered martensite	206

Table 2. Microstructure and HV30 of Q+T 42CrMo4 steel grades

# Annealed and normalized 42CrMo4 steel

Fig. 4 shows the SEM micrographs of annealed and normalized 42CrMo4 steel grades under a magnification of 1000x.



Fig. 4. SEM micrographs (1000x) of annealed and normalized 42CrMo4 steel grades. (a) FC845, (b, c) FC1050, (d) AC845 and (f) AC1050

A ferrite-pearlite microstructure is observed in both annealed grades. However, the prior austenitic grain size (PAGS) of the steel austenitized at a higher temperature (FC1050) is considerably higher, as can be noticed in Fig. 4(b and c). A complex microstructure, composed by bainite with some fractions of ferrite and pearlite, which conferred these steel grades a significantly greater hardness (Table 3), is observed on both normalized grades, AC845 and AC1050. The latter, also presents a coarser microstructure due to the higher austenitization temperature.

Steel grade	Microstructure	Hardness, HV30
FC845	Ferrite-pearlite	183
FC1050	Ferrite-pearlite	210
AC845	Bainite-ferrite-pearlite	301
AC1050	Bainite-ferrite-pearlite	285

Table 3. N	licrostructure and	HV30 of	annealed a	and normalized	42CrMo4	steel grades
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# Hydrogen diffusion

# Quenched and tempered 42CrMo4 steel

As an example, Fig. 5 and Table 4 show the results of the permeation tests performed on QT700-7d steel. Fig 5. represents the recorded permeation current,  $J_p$ , on all the applied stepped transients. The different transients were produced by increasing the cathodic density current from 0.5 mA/cm<sup>2</sup> up to a final value of 6.0 mA/cm<sup>2</sup>. Table 5 shows the values of the applied cathodic current density,  $J_c$ , the steady state of the permeation current density,  $J_{ss}$ , the time

needed to reach  $J_{0.63}$ ,  $t_{lag}$ , and the apparent hydrogen diffusion coefficient,  $D_{app}$ , calculated in each transient.

It is important to note that as the current density increased, the steady-state  $J_{ss}$  also increased proportionally, as more hydrogen was introduced in the steel microstructure. In addition, it is also noted that the first  $D_{app}$  was always the lowest as all hydrogen microstructural traps are empty (first transient), increasing until a maximum and constant value was reached in the last transients,  $D_L$ , which means that all the hydrogen traps were saturated with hydrogen at this point.



Fig. 5. Evolution of the permeation current density over time for QT700-7d steel ( $J_c = 0.5+0.5+1+1+1+1$  mA/cm<sup>2</sup>)

Transient	J <sub>c</sub> [mA/cm <sup>2</sup> ]	J <sub>ss</sub> [µA/cm <sup>2</sup> ]	t <sub>lag</sub> [s]	$D_{app}[m^2/s]$
1	0.5	40.3	1135	$1.27 \times 10^{-10}$
2	1.0	68.2	495	2.91×10 <sup>-10</sup>
3	2.0	108.0	342	4.21×10 <sup>-10</sup>
4	3.0	141.4	297	4.85×10 <sup>-10</sup>
5	4.0	168.3	275	5.24×10 <sup>-10</sup>
6	5.0	197.4	233	6.19×10 <sup>-10</sup>
7	6.0	221.7	235	6.13×10 <sup>-10</sup>

Table 4. Results obtained in the permeation tests carried out on the QT700-7d steel

The obtained results on all the Q+T steel grades are shown in Fig. 6, where it is shown the evolution of the diffusion coefficient with the applied cathodic current density. In addition, Table 5 shows the values of  $D_{app}$ , calculated in the first transient (traps empty) and  $D_L$ , calculated in the last transients (filled traps).



Fig. 6. Representation of D<sub>app</sub> vs. J<sub>c</sub> for the quenched and tempered 42CrMo4 steel grades

Table 5. Apparent (D<sub>app</sub>) and lattice (D<sub>L</sub>) hydrogen diffusion coefficients of quenched and tempered 42CrMo4 steel grades

Steel grade	$D_{app} [m^2/s]$	$D_L [m^2/s]$
QT600-3min	3.43×10 <sup>-11</sup>	8.78×10 <sup>-11</sup>
QT600-30min	5.42×10 <sup>-11</sup>	$1.61 \times 10^{-10}$
QT600-2h	7.71×10 <sup>-11</sup>	$4.27 \times 10^{-10}$
QT600-24h	$1.15 \times 10^{-10}$	5.22×10 <sup>-10</sup>
QT600-7d	$1.27 \times 10^{-10}$	6.19×10 <sup>-10</sup>
QT725-4h	$1.43 \times 10^{-10}$	1.16×10 <sup>-9</sup>

In view of the obtained results, it is worth to note that the shorter the tempering time, the lower the value of  $D_{app}$  for any given  $J_c$  value, which means that the density of hydrogen traps increases with the hardness of the steel. Regarding the value of  $D_L$ , it also increases with the tempering time, as the lattice distortion is reduced.

The grade tempered at 725°C for 4h has the highest  $D_{app}$  and  $D_L$  values, which, in line with the microstructural observations and hardness measurements, indicates the lowest lattice distortion and dislocation density and thus the lowest density of hydrogen traps.

#### Annealed and normalized 42CrMo4 steel

The results obtained with the annealed and normalized steel grades are displayed in Fig. 7 and Table 6. Ferrite-pearlite microstructures (furnace cooled, FC) always had higher hydrogen diffusion coefficients than bainitic, air cooled ones (AC), this fact being associated to their higher hardness and thus dislocation density. On the other hand, the effect of modifying the austenitizing temperature (prior austenitic grain size) was minimal and only in the case of the first D<sub>app</sub> measured on the normalized grades a small variation was detected.



Fig. 7. Representation of Dapp vs. Jc for the annealed and normalized 42CrMo4 steel grades

Table 6. Apparent (D<sub>app</sub>) and lattice (D<sub>L</sub>) hydrogen diffusion coefficients of annealed and normalized 42CrMo4 steel grades

Steel grade	$D_{app} [m^2/s]$	$D_L [m^2/s]$
FC845	$2.24 \times 10^{-10}$	1.15×10 <sup>-9</sup>
FC1050	$2.16 \times 10^{-10}$	1.01×10 <sup>-9</sup>
AC845	5.63×10 <sup>-11</sup>	6.19×10 <sup>-10</sup>
AC1050	1.36×10 <sup>-10</sup>	6.24×10 <sup>-10</sup>

# DISCUSION

Fig. 8(a) and (b) show, respectively, the relationship between steel hardness, HV30, the apparent hydrogen diffusion coefficient,  $D_{app}$ , and the lattice diffusion coefficient,  $D_L$ .



Fig. 8. Relationship between hydrogen diffusivity and steel hardness. (a) D<sub>app</sub> vs. HV30 and (b) D<sub>L</sub> vs. HV30

The relationship of  $D_{app}$  with the steel hardness seems to be independent on the steel microstructure, but in the case of  $D_L$ , normalized microstructures (mainly bainite) gave results a little bit higher than the rest (pearlite and tempered martensite microstructures).

#### CONCLUSIONS

Annealing, normalizing and quench and tempering heat treatments were carried out onto hot rolled plates of a 42CrMo4 steel in order to obtain ferrite-pearlite, bainite and tempered martensite microstructures as to study their influence on hydrogen permeation by means of partial build-up permeation transients.

In all these tests, the  $D_{app}$  associated to the first permetion transient, was always the lowest as all hydrogen microstructural traps present in the steel are empty.  $D_{app}$  increased until a maximum and constant value was reached in the last transients,  $D_L$ , when all the hydrogen traps were already saturated with hydrogen.

 $D_{app}$  and  $D_L$  values are strongly related with the hardness of the steel, having a low dependence on the steel microstructure. Hardness measurement is an easy and practical way to quantify the hydrogen traps present in the steel, which is the feature that most affects hydrogen permeation in iron lattices.

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# **CONFERENCE PAPERS**

# I.7. Fusion energy, nuclear fission and radiation protection

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# SENSITIVITY AND UNCERTAINTY ANALYSIS OF K<sub>EFF</sub> DUE TO NUCLEAR DATA UNCERTAINTIES USING THE SCALE6.2 AND THE MCNP6 MONTE CARLO TRANSPORT CODES

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#### ABSTRACT

The sensitivity analysis is one of the tools that has proven its efficiency to quantify the importance/weight of the physical phenomena at play in the reactor. In this work, we compare different schemes of sensitivity calculation, based on first-order-linear perturbation theory: the IFP "Iterated Fission Probability" method which was implemented in the MCNP6 code, and the CLUTCH "Contribution-Linked eigenvalue sensitivity/Uncertainty estimation via Tracklength importance Characterization" method which was developed in the SCALE6.2 code. The sensitivity results obtained from the both approaches were evaluated and confirmed through the reference direct perturbation sensitivity calculations. This paper also aims to estimate the uncertainties of the  $k_{eff}$  due to nuclear data in order to increase the safety of nuclear systems.

Generally speaking, the various sensitivity calculation schemes, for each of the problem cases "Benchmarks", are in good agreement. Moreover, the greatest contribution of nuclear data uncertainties in the effective multiplication factor ( $k_{eff}$ ) came from the fission reactions of <sup>235</sup>U, the <sup>238</sup>U absorption cross sections as well as the moderator scattering.

Keywords: Sensitivity, Nuclear data uncertainty, SCALE6.2, MCNP6, linear perturbation theory.

#### **INTRODUCTION**

Sensitivity/uncertainty (S/U) techniques have become increasingly important in the criticality safety analysis, in aims to accomplish the further reducing nuclear data uncertainties observed in reactor safety parameters for some nuclides-reactions.

In this paper, the sensitivity and uncertainty analysis have been performed for two benchmark experiments taken from the International Handbook of Evaluated Criticality Safety Benchmark Experiments (IHECSBE) [1]. In general, the Benchmark experiments are categorized according to their fissile media (Plutonium, HEU, LEU etc.), their physical form (metal, compound, solution, etc.), their neutron energy spectrum (thermal, intermediate, fast, and mixed spectra) and a three digit reference number [1][2]. However, this research involving only two different types of benchmarks:

- HEU-COMP-THERM-002: Highly Enriched Uranium Compound Thermal.
- HEU-MET-FAST-022: Highly Enriched Uranium Metallic Fast.

Therefore, an overview of the most important neutron's behaviours that occurs under each of these critical cases will be investigated, when examining the energy-dependent sensitivity coefficients for the major pairs nuclides-reactions contributing in both problem cases. Moreover, the sensitivity and uncertainty results were generated, using the SCALE package [3] [4] [5] and MCNP code [6], based on the first perturbation theory [7] (IFP [6][8] and CLUTCH [9] [10][11] approaches) in the continuous energy mode. On the other side, to ensure the accuracy of our analysis, these results are confirmed through the use of the reference direct perturbation methodology within the Multigroup TSUNAMI-3D simulations [3]. This conventional method would add a lot more weight and validity to our sensitivity/uncertainty calculations.

#### MATERIALS AND METHODS

#### **Benchmark Test Experiments**

#### HEU-COMP-THERM-002

Critical experiments of hexagonal graphite rods containing highly enriched uranium moderated and reflected by water were performed at Oak Ridge National Laboratory (ORNL)[1].

A total of 25 critical assemblies were constructed, using two fuel element types, one designated as NRX-A3 and the other as NRX-A4, to provide data for criticality safety analyses [1]. Except for differences in the uranium content, both fuel element types (NRX-A3 and NRX-A4) had the same composition. The uranium was enriched to 93.15 wt.% <sup>235</sup>U. The average bead diameter was 0.003 in. whereas the average thickness of the pyrolytic graphite coating was 0.001 in. The fuel elements were hexagonal cylinders with a measurement of 0.754 in. (0.435-in. sides, 0.870-in. diagonal) containing 19 uniformly spaced longitudinal holes [1]. The 19 holes were 0.096 in. in diameter for the NRX-A3 elements and 0.099in. in diameter for the NRX-A4 elements. The center hole was slightly enlarged at both the top and bottom [1].

The NRX-A3 elements surrounded the NRX-A4 elements in "rounded" lattices. Each lattice configuration was filled with water until criticality was achieved [1]. Moreover, the water-moderated and -reflected triangular lattices were surrounded each fuel element as well as filled all 19 longitudinal holes in the element Fig. 1.

All 25 experiments are considered acceptable for use as benchmark experiments. However, in this paper only the first case was considered.



view.

Fig. 1. 2D and 3D view of HEU-COMP-THERM-002, SCALE model.

# HEU-MET-FAST-022

Duralumin-reflected spherical assembly of <sup>235</sup>U(90%) was conducted by VNIIEF in 1962 at its criticality test facility (CTF). This experiment provides an acceptable layered spherical critical benchmark model [1].

The critical assembly is a sphere with a core of  $^{235}$ U(90%) metal having a central cavity and Duralumin reflector [1]. The assembly is represented by the following two models [1][12]:

• The first model is a detailed model with the core is composed of 9 adjacent spherical layers of 8.35-cm outer radius and a single-layer Duralumin reflector with an outer radius of 12.25 cm Fig. 2. The proportion between the most abundant uranium nuclides in the core layers <sup>235</sup>U and <sup>238</sup>U was approximately 90.4% and 9.5%, respectively [1]. The percentage of the <sup>235</sup>U isotope in the core parts was known with 0.17% of relative error. The impurity composition in the uranium units was dominated by three elements, Fe, C, and W. Table 1 gives a more detailed description of the core-layer material.

_	Composition, wt.%							
Layer No.	<sup>234</sup> U	<sup>235</sup> U	<sup>238</sup> U	impurity				
1	1.08	89.47	9.25	0.2				
2	1.07	89.44	9.09	0.4				
3	1.14	88.8	9.71	0.35				
4	1.14	88.86	9.69	0.31				
5	1.15	88.74	9.75	0.36				
6	1.09	89.34	9.28	0.29				
7	1.09	89.25	9.32	0.34				
8	1.08	89.48	9.2	0.24				
9	1.1	89.28	9.37	0.25				

Table 1. Characteristics of the Spherical Core Layers.

The reflecting material used by the assembly was Duralumin, which contained Al, Fe, and Cu in a mixture with weight proportions of 92.4%, 3.5% and 4.1%, respectively [1].

• The second model is a simplified model with the core homogeneous in composition and the same Duralumin reflector as described above.

For this research, we are considered the detailed model as seen in Fig. 2.



Fig. 2. 3D view of f HEU-COMP-THERM-002, SCALE model.

# Methodology

During this research, the experimental benchmarks were developed in three-dimensional geometry within the SCALE package and the MCNP code.

For the CE TSUNAMI-3D/SCALE simulations, the Contributon-Linked eigenvalue sensitivity/Uncertainty estimation via Tracklength importance Characterization (CLUTCH) approach is selected to generate the sensitivity vectors. This method greatly reduces the run time of the sensitivity coefficient calculation at no expense to its accuracy [10]. Additionally, a mesh grid has been generated in which the F\*(r) weighting function must be distributed to ensure the convergence of the fission source [14].

For the KSEN/MCNP calculations, the Iterated Fission Probability methodology is used to calculate sensitivity coefficients. This capability is specifically designed to use in continuousenergy calculations. Therefore, the sensitivity vectors are performed in a single forward calculation. Although this approach is useful for benchmarking the accuracy of other sensitivity coefficient methods [3] [11], the method frequently produces a large memory footprint because it requires the storage of region, isotope, reaction, and energy-dependent reaction rates for every particle for some number of generations.

The accuracy of the energy-integrated sensitivity coefficients can be confirmed by generating the reference direct perturbation sensitivity coefficients. This technique is provided in the MG TSUNAMI-3D sequence. Further, this module computes also the implicit effects of resonance self-shielding calculation [13]. Hence, the direct perturbation sensitivity of  $k_{eff}$  to the number density of each nuclide-reaction is obtained within the two benchmark cases. These sensitivities of  $k_{eff}$  to the number density are equivalent to the sensitivity of  $k_{eff}$  to the total cross section integrated over energy [3]. The direct perturbation results will require much more simulation time than the other CE methodology needs (IFP and CLUTCH), because this approach performed separate forward and adjoint Monte Carlo transport calculations [3].

Furthermore, all sensitivity calculations performed in this study, with both codes, use the ENDF/B-VII.1 library and the default 56groupcov7.1 covariance matrix provided by the SCALE package. As well, all these calculations are simulated on a computing cluster, which contains uniform-speed computational nodes.

The Monte Carlo calculations for each problem are simulated the same number of active neutron histories, and thus all the simulations used  $10^6$  neutrons per cycle in 1100 active cycles (the first 100 cycles are skipped). In the SCALE simulations, we used 21 MPI processors, whereas 35 MPI tasks are used in the MCNP calculations. Table 2 summarizes the time needs to generate the sensitivity vectors for both benchmark cases.

Table 2. Benchmarks runtime comparison					
Benchmark cases	IFP MCNP	CLUTCH SCALE	SCALE Direct Perturbation		
HEU-COMP-THERM-002	12h	52h	38h		
HEU-MET-FAST-022	2h	12h	12h		

# **RESULTS AND DISCUSSION**

## **K**<sub>eff</sub> calculations

To improve the reliability of our calculations, the effective multiplication factor result ( $K_{eff}$ ) for the both Benchmark cases, studies in this paper, are given in Table 3. This result has been compared with the experimental values of  $K_{eff}$  which are taken from the handbook *ICSBEP* [1].

Table 3. Effective multiplication factor k<sub>eff</sub> of the selected benchmarks and their statistical uncertainties

Relative Relative SCALE Relative Benchmark IFP difference CLUTCH difference Direct difference									
cases MCNP (%)* SCALE (%)* Perturbation (%)* IHECSBE	Benchmark cases	IFP MCNP	Relative difference (%)*	CLUTCH SCALE	Relative difference (%)*	SCALE Direct Perturbation	Relative difference (%)*	IHECSBE	
HEU-COMP-1.00811.01081.00991.0011THERM-002 $\pm 0.0000$ $0.70\%$ $\pm 0.0000$ $0.97\%$ $\pm 0.0000$ $0.88\%$ $\pm 0.0069$	HEU-COMP- THERM-002	$\begin{array}{c} 1.0081 \\ \pm \ 0.0000 \end{array}$	0.70%	$\begin{array}{c} 1.0108 \\ \pm \ 0.0000 \end{array}$	0.97%	1.0099 ± 0.0000	0.88%	1.0011 ± 0.0069	
HEU-MET-       0.9976       0.9976       0.9949       1.0000         FAST-022 $\pm$ 0.0000       0.24% $\pm$ 0.0000       0.24% $\pm$ 0.0000 $\pm$ 0.0019         * Polating difference = (//k	HEU-MET- FAST-022	$0.9976 \pm 0.0000$	0.24%	0.9976 ± 0.0000	0.24%	0.9949 ± 0.0000	0.51%	$1.0000 \pm 0.0019$	

As seen in Table 1, the relative difference in  $K_{eff}$  values between the tree calculation methods and the experimental values is less than 0.1% for the thermal benchmark (HCT002), and it is reduced to 0.51% when examine the fast critical experiment (HMF022).

# Sensitivity profiles

The sensitivity coefficients results are provided, in this section, based on the method described previously in section 2.2.

Table 4 and Table 5 present the energy-integrated sensitivity coefficients to various nuclear data (fission, capture, scattering) for the major nuclides contributing in the two critical experiments: HEU-COMP-THERM-002 and HEU-MET-FAST-022, respectively. Further, Fig.3 and Fig. 4 graph the  $k_{eff}$  sensitivity profiles for either major isotopes - reactions contributing in these benchmark cases.

The sensitivity vectors, as mentioned earlier, have been calculated over 252 energy groups using the ENDF/B-VII.1 cross section library. Moreover, these results compare two different sensitivity coefficient generation methods (IFP and CLUTCH) with the reference direct perturbation sensitivity coefficients in order to evaluate and increase the accuracy of our sensitivity calculations.

Table 4. Energy	and region integrated sensitivity coefficients for the major nuclide-reaction
contributing in	HEU-COMP-THERM-002.

Nuclide / Reaction	MCNP IFP	% Std. Dev. *	SCALE CLUTCH	% Std. Dev. *	SCALE Direct Perturbation	% Std. Dev.*
U-235 fission	0.23183	0.12%	0.23170	0.00%	0.23325	0.02%
U-238 capture - H-1 elastic	-0.00493 0.45303	0.17% 0.42%	-0.00494 0.45539	0.03% 0.41%	-0.00414 0.32265	0.02% 0.51%



(a)  $^{235}$ U fission sensitivity coefficients.



(b)  $^{238}$ U capture sensitivity coefficients.



(c) H-1 elastic sensitivity coefficients.

Fig. 3. Energy-dependent sensitivity of  $k_{eff}$  for the major nuclides-reactions contributing in HEU-COMP-THERM-002.

Nuclide / Reaction	MCNP IFP	% Std. Dev.*	SCALE CLUTCH	% Std. Dev.*	SCALE Direct Perturbation	% Std. Dev.*
U-235 fission	0.63463	0.03%	0.63454	0.00%	0.59366	0.03%
U-238 capture	-0.00279	0.02%	-0.00278 0.07248	0.01%	-0.00305	0.04% 13.86%

Table 5. Energy and region integrated sensitivity coefficients for the major nuclide-reaction contributing in HEU-MET-FAST-022.



(d) <sup>235</sup>U fission sensitivity coefficients.



(e) <sup>238</sup>U capture sensitivity coefficients.



(f) <sup>27</sup>Al elastic sensitivity coefficients.



As shown in Table 4 and Table 5, the IFP and CLUTCH methods for generating sensitivity coefficient are in good agreement with the direct perturbation results for some nuclides-reactions but not for others. This discrepancy is expected and is due to neglecting the implicit effect in the CE sensitivity methods because these approaches do not require resonance self-

shielding calculations. This contribution became more important for resonance reactions where self-shielded multigroup cross sections are strongly affected.

The thermal nature of the neutron spectrum in the HCT critical experiment is apparent when examining the sensitivity coefficients (Fig.3a through 3c). The <sup>235</sup>U fission sensitivity reaches a maximum value in the thermal energy range where the highest fission events occur.

The high peaks of the <sup>238</sup>U capture sensitivity related to scattering reactions allowing neutrons to escape from the large <sup>238</sup>U absorption resonance range ([6.76ev - 400 ev]) and increase the contribution of these neutrons in the fission reactions.

The sensitivity of  $k_{eff}$  to <sup>1</sup>H elastic scattering reflects the structure of other nuclides, especially the <sup>238</sup>U. In fact, the moderator scattering is positive for the fast energies because scattering reaction at these energies prevent fast neutrons from leaking out of the system, while the thermal scattering low S( $\alpha$ , $\beta$ ) contributes with a negative fraction of response in the thermal region.

On the other hand, the same behaviours of the HCT problem (Fig.4d through 4f) are observed in the next benchmark case "HEU-MET-FAST-022". However, in this case, the multiplication factor is more sensitive to the fission parameters of  $^{235}$ U, the capture cross section of  $^{238}$ U, and the scattering cross section of  $^{27}$ Al in faster energies (above 10<sup>4</sup> eV).

#### Nuclear data uncertainty

The SCALE 56 groupcov7.1 covariance data library is applied to the sensitivity coefficients for the two benchmark cases, in order to quantify the uncertainty in  $k_{eff}$  due to nuclear data uncertainty. Fig. 5 and 6 present the great uncertainties in  $k_{eff}$  within the both thermal and fast critical problems, respectively. Additionally, a numerical description of these results are cited in Table 6.



Fig. 5. HEU-COMP-THERM-002 uncertainty quantification.





HEU-MET-FAST-022	uncertainty	quantification.
------------------	-------------	-----------------

	Nuclide / Reaction	MCNP IFP	SCALE CLUTCH	SCALE Direct Perturbation
	U-235			
1 P-	Fission;fission	0.07108	0.07108	0.07232
02 INV	U-238			
THE P	N_gamma;n_gamma	0.00492	0.00492	0.00406
2 BI F	H-1			
T-0.	elastic;elastic	0.18452	0.18452	0.1184
FAS	U-235			
HEU-MET-J	Fission;fission	0.26049	0.26048	0.24374
	U-238			
	N gamma:n gamma	0.00276	0.00275	0.00301
-	11	0.00270	0.00270	0.00001
	Al-27	0.05460	0.05(10	0.00414
	Elastic;elastic	0.25462	0.25613	0.00414

Table 6. The uncertainty information of  $k_{eff}$  (%  $\Delta k/k$ )

As it is shown in Fig. 5 and Fig. 6, the  $^{235}$ U fission reaction, the  $^{238}$ U capture cross sections, and the moderator scatter (<sup>1</sup>H or  $^{27}$ Al), for each critical experiment, have the greatest contribution to uncertainties in the effective multiplication factor. The high contributions of the uncertainties in k<sub>eff</sub> are due to the important sensitivity profiles computed for these nuclides-reactions.

#### CONCLUSION

Transport calculations of responses such as the effective multiplication factor inherently have biases and uncertainties due to several factors that can be grouped into three classes: numerical approximations in the transport code, system modelling approximations, and input data uncertainties. However, the major source of uncertainty in the calculated response is due to uncertainties in evaluated nuclear data. Therefore, the sensitivity and uncertainty analysis is mainly conducted to quantify exactly the uncertainty in  $k_{eff}$  due to the nuclear data uncertainty. All other error sources can be enhanced in order to minimize the discrepancy between calculation and experiment.

This research presents a comprehensive study of sensitivity/uncertainty analysis for two different experimental benchmarks in order to quantify the importance/weight of various nuclear data parameters. All the calculation results provided in this work have been made with the SCALE 6.2 and MCNP 6.2 codes using the ENDF/B-VII.1 cross section library and the default 56groupcov7. 1 covariance matrix provided by the SCALE package.

In terms of the  $K_{eff}$  results, the relative differences between calculations and experiments results remain smaller than 0.1% for the critical thermal benchmark (HEU-MET-FAST-022), and it was less than 0.51% in the fast benchmark case (HEU-MET-FAST-022).

Moreover, the sensitivity profiles have been performed over 252 energy groups for the both critical benchmarks. These sensitivity vectors indicate important nuclide-reactions that appear in the thermal and fast problem cases. The accuracy of our analytical results was confirmed through the use of reference direct perturbation sensitivity calculations. Furthermore, the greatest contribution of nuclear data uncertainties in the effective multiplication factor (k<sub>eff</sub>) came from the fission reactions of  $^{235}$ U and the absorption of  $^{238}$ U as well as the moderator scattering ( <sup>1</sup>H or <sup>27</sup>Al).

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# WCLL AND HCPB MODELS ACTIVITY COMPARISON OF DIVERTOR REFLECTOR AND LINEAR PLATES

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One of the primary goals of EU DEMO (European demonstration fusion power plant) is tritium selfsufficiency and efficient neutron multiplication. After years of investigation, two breeder blanket concepts are being considered the Helium Cooled Pebble Bed (HCPB) and Water Cooled Lithium-Lead (WCLL). Differences are due to materials' choice, which affects tritium breeding and neutron-induced activities of important components.

In this work, neutron-induced activities were calculated for divertor liner and reflector plates. The comparison was made using the same divertor geometry but two different breeding blanket concepts. Linear and reflector plates are made of 3 materials: Eurofer, tungsten, and water. Eurofer and tungsten protect vacuum vessels, magnets, and cooling components under plasma-facing components from neutrons, alpha particles, thermal effects, and impurities. At divertor, water is used as a coolant.

For these calculations was used FISPACT – II and for activation reactions, cross-sections, and nuclear reactions was used TENDL – 2017 nuclear data. The considered time of operation is the first EU DEMO scenario. At this operation, a reactor is working 5.2 years continuously at 30% of nominal power and the end ten days pulsed operation. One pulse consists of 4 hours of full-power operation and 1 hour not working. After the operation activities, results were calculated up to 1000 years, and the main radionuclides were identified.

Calculations results of main radioisotopes showed that <sup>55</sup>Fe, <sup>56</sup>Mn, <sup>187</sup>W, <sup>16</sup>N has the main influence on the total activity at the beginning of cooling time and <sup>55</sup>Fe, <sup>185</sup>W and <sup>14</sup>C at the end of cooling time. The neutron-induced activity showed that total activity is average 1.19 times higher when a breeding blanket concept is WCLL.

Keywords: Fusion, DEMO, HCPB, WCLL, FISCPACT, activity

# UNCERTAINTY AND SENSITIVITY ANALYSIS OF THE PHEBUS FPT1 TEST SIMULATION RESULTS

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#### ABSTRACT

The PHEBUS program is an example of an international cooperative research program providing valuable data for validating severe accident analysis computer codes. One of the main objectives of the PHEBUS program is to study the process in the bundle of the light water reactors during severe accident conditions as well as the release, transport, and retention of fission products.

In this article the PHEBUS - FPT1 test will be analysed in more detail, focusing on the late phase of bundle degradation. Best estimate simulations are provided using best estimate, severe accident code - RELAP/SCDAPSIM. However, the simulation of processes in the nuclear installation during accidents is attended with many uncertainties. There are three major sources of uncertainties: code or model uncertainty, representation or simulation uncertainty, and plant (installation) uncertainty. This article is focusing on the uncertainties which come from the initial parameters and boundary conditions.

Uncertainty analysis was performed using the GRS methodology together with SUSA statistical tool. GRS methodology is based on Monte-Carlo methods for randomize uncertain parameters and it is an application for Wilks' formula. For the uncertainty analysis it was decided to use 95% probability content and 95% of confidence level with two-sided tolerance limit. For the uncertainty quantification, two RELAP/SCDAPSIM calculation results are chosen: 1) Cladding temperature in the elevation 950 mm; 2) Total hydrogen generation. Uncertainty upper and lower limits of the calculation results are bounding the experimental data calculation. The upper uncertainty limit covers all experimental data in all phases of the test.

Sensitivity analysis are also provided using SUSA tool. Different correlations could be used to evaluate the influence of the initial uncertain parameters to calculation results. Spearman's rank correlation is used, which is based on the non-parametric method. Determination coefficient ( $\mathbb{R}^2$ ) values were checked before checking the influence of uncertain parameters on calculation results. Determination coefficient ( $\mathbb{R}^2$ ) shows the linearity of uncertain initial parameters to calculation results. In practice, if  $\mathbb{R}^2$  is less than 0.6 the linearity between initial parameters and calculation results is weak and sensitivity analysis may be not exact. In the case of cladding temperature at 950 mm, it has been indicated high value of  $\mathbb{R}^2$ at all phases of the experiment. However, in the case of total hydrogen generation,  $\mathbb{R}^2$  coefficient falls to 0.4 and sensitivity analysis cannot be exact at three different phases: oxidation, power-plateau and heat-up. Spearman's rank correlation showed what thermal conductivity of  $ZrO_2$  is the dominant parameter for the calculation results. Thermal conductivity of  $ZrO_2$  has high negative influence on the calculation results during all test phases.

As it was described before, in the case of total hydrogen generation  $R^2$  has low values at the last 3 test phases. Thus, it was decided to make scatter plots and draw regression lines for thermal conductivity of ZrO<sub>2</sub> on the calculation results of total hydrogen generation at oxidation and heat-up phases. Sample scatter plot and regression line at oxidation phase showed non-linear correlation or no correlation between ZrO2 thermal conductivity and calculation results of hydrogen generation. However, at the heat-up phase it was indicated a negative influence of  $ZrO_2$  thermal conductivity on the calculation results of hydrogen generation.

Using experience gained form the application of uncertainty and sensitivity analysis it will be possible to update the model to get more accurate simulation results of the PHEBUS - FPT1 test.

Keywords: Severe accidents, Uncertainty and Sensitivity, PHEBUS - FPT1

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# **EVALUATION METHOD OF DATA-DRIVEN SOLUTIONS TO DISRUPTIVE CHALLENGES IN THE ENERGY SECTOR**

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#### ABSTRACT

The distribution and energy trader companies are currently undergoing transformations which are based on the increasing low emission production, digitization, liberalization, etc... These transformations bring disruptive challenges on the side of users, technologies, business and legal. The aim of this paper is to take a closer look at these challenges and categorize them based on their effects. The other goal of this research is to build an evaluation system that examines these disruptive challenges from the perspective of the Electricity Utilities and assesses the possibility of data-driven solutions. The evaluation method of the disruptive challenge, exploration of possible solutions, is it possible to convert the problem to a data-driven task, how to fit the task into the conceptual data model? Based on the results of these processes it is possible to present data-driven solutions to the challenges, and it allows to select the data sets that would be used in a Proof-of-Concept project.

**Keywords**: energy sector, disruptive challenges, data analysis, data-driven approach, conceptual data model, data sets

#### **INTRODUCTION**

Energy transitions are complex technological, economic and social process. Nowadays, this classic energy supply chain is undergoing transformations because of the technological developments. The exact outcome of it is difficult to predict due to the emergence of decentralized power generation units, the spread of electric cars, changing environmental conditions and changing consumer thinking and needs. The changes include weather-dependent energy production, re-feeding to the grid at low voltage levels, increasing demand during night-time due to the charging of electric vehicles. Changes are already in course posing new challenges to European Electricity Utilities [1].

In a 2016 survey, energy company executives were asked what the main changes are that will determine how the sector will work in the future. Four key trends were identified [2]:

-The locations and opportunities for energy production are constantly changing

-New energy innovations will become feasible over the next two decades

-Decentralised energy production makes the development of smart grids unquestionable

-Advanced information and communication technology (ICT) systems and Big Data-based optimizations will play a prominent role in the future

The changes are seen by all energy companies and in some way, they want to play a role in the solutions or take the opportunities. There are also new competitors on the market, technology companies such as TESLA, who can provide a full service for home energy supply and transportation. In order for European Electricity Utilities to be able to prepare for these transformation processes, they need to be aware of the changing environment and need more information about their local environment.

The aim of this paper is to build an evaluation system that examines these disruptive challenges from the perspective of the Electricity Utilities and assesses the possibility of datadriven solutions. The paper is structured as follows: the next section presents an overview of the disruptive challenges in the energy sector; Section 3 describes the evaluation method of the challenges from the perspective of possible data-driven solutions. Section 4 presents a use case and show how to use the evaluation method on a fault correction problem. Finally, Section 5 summarizes the conclusions of the paper.

#### DISRUPTIVE CHALLENGES IN THE ENERGY SECTOR

Definition of disruptiveness in the energy sector was not found in the relevant literature, that is why it has been created. To determine the meaning of distruptivity in the energy sector, the basic definition of disruptivity and the definition of energy Trilemma were used.

World of business defines a disruptive innovation or technique as it has a rapid and major effect on technologies that existed before and this kind of innovation creates a new market and value network. For example, the emergence of low-priced car models had a disruptive effect on the market for horse-down vehicles and changed the transportation market in early 1900s [3].

The energy sector is currently undergoing a major transformation, driven by the need for sustainable development. The European Union is committed to this direction, and a number of provisions have been included in the Climate and Energy Packages. At the heart of these goals is to secure a healthy energy system that can be achieved through the management of three dimensions of the Energy Trilemma (Fig. 1) [4]:

Energy SecurityAffordabilityEnvironmental Sustainability

Energy Security measures a nation's capacity to meet current and future energy demand reliably, withstand and bounce back swiftly from system shocks with minimal disruption to supplies. The dimension covers the effectiveness of management of domestic and external energy sources, as well as the reliability and resilience of energy infrastructure.

Affordability assesses a country's ability to provide universal access to reliable, affordable and abundant energy for residential and commercial consumers. The dimension includes basic access and affordability to electricity, fuels and technologies, energy consumption to promote prosperity.

The environmental sustainability of energy systems represents the transition of the country's energy system towards mitigating and avoiding potential environmental damage and the effects of climate change. The dimension focuses on the efficiency of production, transfer and distribution, decarbonisation of energy supply and air quality.

# THE ENERGY TRILEMMA



Fig. 1. Three main pillars of Energy Trilemma [5]

Disruptive challenges in energy supply mean that technologies, ideas or innovations are developed that affect or endanger the fulfilment of the three dimensions of the Energy Trilemma (Energy Security, Affordability, Environmental Sustainability).

The challenges come only partially from the field of energy. Thanks to the development of society and technology, other industries also have a strong impact on the future of Electricity Utilities. These areas have been analysed on the basis of literature research [1,6,7,8]. As a result, the main causes of disruptive challenges to the energy sector can be divided into five groups:

- -Development of energy technologies
- -Innovations in Information and Telecommunication sectors
- -The emergence of new business models and habits
- -Changing consumer habits and demands
- -Changes in the regulatory environment

The second figure shows the additional directions that can be broken down in each group. These innovations, technologies and changes are most often not mean a challenge to the energy sector on their own, rather the members within each group reinforcing each other and appear as a challenge together. An example of this is the continued spread of distributed energy resources (DER) production, which is possible due to the development of energy technologies. On top of that, it also requires consumers to commit to sustainable awareness and deploy PV panels to their rooftop. That means changing consumer habits and demands. In addition, the regulatory environment provides support for the rapid installation of DER. On the one hand, this helps to achieve sustainability goals in the Energy Trilemma, but it can lead to a number of local problems in the field of energy security, so it is certainly a disruptive challenge by definition, which Utility companies will have to face in the short-term future.



Fig. 2. Grouping of disruptive energy challenges [1,6,7,8]

# **EVALUATION METHOD OF DATA-DRIVEN SOLUTIONS**

Energy companies have also begun to address disruptive challenges, as the transformation of the market and supply chains can lead to market losses for the benefit of new entrants. It is therefore important to evaluate an upcoming problem or challenge in the order to identify the effects of the problem. It is also a matter for current companies whether the challenges hold opportunities or threats for them.

Agility and speed are very important advantages for new market players and start-ups, which are difficult for a multinational company to compete with. That is, if a new player identifies a problem well, it can quickly solve it. That's what the energy companies have to compete with. However, the classic energy sector also has its own advantages against speed, which are based on experience and great amount of historical data. The Energy Utilities have a lot of data about their customers, how their networks work, and its typical failures. In addition, the spread of smart meters is producing a wealth of measurement data. This amount of data is still only partially exploited in the sector today. For this reason, there is a very large potential in the search for data-driven solutions, which builds on data science and the use of artificial intelligence.

The purpose of this chapter is to present an evaluation method that helps to identify a possible data-driven solution to answer a disruptive challenge. This process has been developed by the authors. As a result of this technique, the Utilities will be able to decide whether a data-driven solution is available to solve a specific problem and whether it is a good idea to start a proof of concept project on that issue.

The four steps of evaluation method of data-driven solutions:

- -Identify the effects of the disruptive challenge
- -Explore possible solutions
- -Is it possible to convert the problem to a data-driven task?
- -Does the energy company have relevant data set for the task

*The first step* is to evaluate the impact of the challenge. The impact of the problem on traders, the grid and consumers should be examined, as well as its legal aspects. Mapping these effects contributes to deciding whether a problem violates a dimension of energy Trilemma,

whether it is disruptive change. After that, it should be analysed whether the challenge poses a threat or opportunity to the Electricity Utilities. A threat occurs when a start-up can solve the examined challenge without any contribution with a classic energy company. This can cause that the company's revenue or market share to decrease with the emergence of a new market player. If technological development is implemented that only the energy company can make, it should be determined as an opportunity.

*The second step* is to examine the possibilities in which the problem can be solved. It is worth doing literature research or interviewing experienced professionals. Technological, human resources and financial differences may also emerge between the identified solutions. Data-driven answers can benefit from this because instead of hardware solutions, you don't need to install expensive physical devices.

*In the case of the third step*, it is examined which of the solution options contains at least partly data-driven answers to the challenge. Data-driven solutions need to be further examined for the aspects of data maturity. (Figure 3.) The data maturity model identifies four types of analytics [9]:

-Descriptive Analytics -Diagnostic Analytics



Fig. 3. The data maturity model [9]

*Descriptive analytics* uses data to describes what happened in the company. It is often used to get an insight into the performance of the company in the past. For example, for an energy company, this can be an overview of the monthly consumption of consumers.

In the *Diagnostic analytics* stage, the focus lies on analysing problems or occurrences in the data. The analyst will need to figure out why such event has happened. For example, the monthly consumption was increased by 15 % because of the sunny, warm weather.

*Predictive analytics* deals with making predictions on what is going to happen based on historical data. This is the first data majority level, where the data-driven solutions can deal with the other solutions. For example, the forecasting of the 15 minutes consumption can be carried out.

*Prescriptive analytics* is the most valuable and hardest form of analytics. This segment of analytics revolves around prescribing decisions and actions to the business. For example, it can be determined which power plant should generate to reach the optimal well being in the system.

Once the data analysis task has been determined based on the maturity levels, *the final step* is to examine whether Electricity Utilities have the necessary data in their data warehouse. To do this, the conceptual data model of the company must be set up based on the data sets of the company. The conceptual data model represents high-level business aspects and provides an overview of distribution network processes [10]. It can be used very effectively in a corporate environment for communication purposes, as it makes it easy to understand and define certain business processes. It allows you to select the data sets that would be used in a Proof of Concept project when planning a data mining project.



Fig. 4. Simplified conceptual data model of Electricity Utilities [11]

Fig. 4 shows the Electricity Utilities' simplified conceptual data model. Based on the core activities of the companies close to the distribution network, a total of 14 data marts can be distinguished, between which there are clearly defined relationships [11].

# **USE CASE FOR THE EVALUATION METHOD**

The developed evaluation method is presented through a possible use case. The new installations of DERs require a new mode of operation from network operators due to the

potential bi-directional energy flow. As a result, new types of faults can occur on the low-voltage network, for example, asset losses due to voltage instability. Furthermore, there is a general trend that the coordinators, who handle fault fixing, are ageing out of the profession. This problem has been analysed according to the 4 steps.

As a first step, it is easy to conclude that the challenge can be interpreted as a disruptive failure, as these events cause individual or group supply interruptions. This problem also has a financial impact, if the faults cannot be rectified in time according to the regulations, then the user will be compensated. The root causes are not entirely traceable to evolving technologies, but the lack of operating staff is at least as much of a problem. This problem is clearly linked to DSOs, so external companies cannot provide a solution to this, meaning it can be interpreted as a development opportunity for the Utilities.

Solutions could include the training of young colleagues as coordinators or purchasing new assembly vehicles and thereby increasing the number of mechanics. There are few online measurement points on the low-voltage network, so new network monitoring systems installation could be a solution too. All of these are expensive and time-consuming answers to a problem. It can also be a goal to increase efficiency during fault fixing.

Efficiency gains can be achieved by supporting the work of the coordinators by preevaluating each reported fault based on a Machine Learning algorithm. This supervisedlearning algorithm is able to determine how long the reported fault is expected to be fixed with a certain probability. This predictive analytics can help the coordinators to decide which order would be optimal to fix the failure.

The final step is to check if there is data available for model building. Data required for such a task: fault report information, date of report, the network location of the fault, information about repair teams, information about fixed faults, consumer data. These are available in the following datamarts: Fault detection and fixing, Network data/GIS (geographic information system), Operation of the system, Asset management, Customer relationships and Measurement centre. The study can be supplemented with an external data source, for example, with historical weather data, thus, force majeure periods can be marked.

Based on the evaluation, it is recommended to start the proof-of-concept (PoC) project of such a predictive recommendation system. Based on this result of PoC can be decided whether the solution provides adequate predictions and can be implemented into its live operation.

#### CONCLUSION

This paper aimed to build an evaluation system that examines the disruptive challenges from the perspective of the Electricity Utilities and assesses the possibility of data-driven solutions. First, the definition of disruptiveness in the energy sector was created and after that, the four-step process was presented as the evaluation method. As a result of this method, it can be decided whether it is possible to start a proof-of-concept project to develop a data-driven solution to a problem.

Through a relevant use case, the methodology was presented. The result of the process confirmed that it is worth to build a predictive model that can determine the faults correction time. Based on this use case, the data analysts and data scientists at European Utilities should consider to use this evaluation method to make a quick decision before a data-driven PoC development.

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# CONVERSION HEAT TO ELECTRICITY VIA MOLECULAR ACTION HEAT ENGINE

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#### ABSTRACT

It is well known that modern energy is based on the thermodynamic conversion of heat to motion or electricity. Thermodynamic action means heating, expanding, cooling and compressing the gas. This paper deals with not thermodynamic but molecular action heat engine. Molecular action means that in our process all thermodynamic parameters of gas remains constant, but the motion of each molecule changes by an external force. This changing of molecular motion gives us the possibility to convert heat to electricity. For creating molecular action, we use gravitation and centrifugal force. All physical effects on which molecular action heat engine is based are described in this paper. The effects are analyzed theoretically and modelled by numerical simulation. The results of numerical simulation of gravitational influence on the molecular motion of gas are presented. Numerical simulation was made both for gravity and centrifugal force. Numerical simulation was also made for different types of gas. We use both 2D and 3D modelling to understand mechanisms of thermal effects. On the basis of numerical simulation, the construction of molecular action heat engine was developed. All parameters of construction are calculated by taking into account all physical factors. The scheme of construction is presented in this paper in all details. The mechanism of engine working is explained.

Keywords: Strong gravity, heat transfer, molecular motion, thermal equilibrium, heat engine

#### **INTRODUCTION**

The first heat engines were built in the XVII century [1]. Firstly they were intended for conversion heat to motion and then for conversion heat to electricity. The steam engine, Sterling's engine, steam turbine, Diesel engine differ one from another, but the main principle remains the same. All these engines are based on thermodynamic action. Thermodynamic action means heating, expanding, cooling and compressing the gas. Despite the fact that many years have passed, the basic mechanism of transforming heat to mechanical or electric power remains the same [2].

The appearance of direct thermoelectric converters [3] did not cause some serious changes in energy. These converters had not been employed in the industry of energy because of low efficiency and high price. Brownian [4], quantum [5], and monatomic [6] heat engines have very small power to be used anywhere. Thus, today, heating, expanding, cooling and compressing the gas is still the main way to transform heat energy into mechanical or electric energy. So it is interesting to find some new method of transforming heat to electricity.

When we heat, expand, cool and compress the gas, we affect it as a whole system. In this study, we affect not gas as a whole system but gas molecules. So we develop not the thermodynamic but molecular engine. We act on gas molecules by gravitation created in the centrifuge. In our processes, thermodynamic parameters of gas always remain constant but only the character of molecular motion changes. This change of molecular motion character gives us the possibility to convert heat to electricity. Thus, our method of heat to electricity conversion is original and interesting.

#### THE MAIN PRINCIPLE FOR THE METHOD

When we throw up the stone, it will slow down with increasing height. No matter what the angle of flight will be, the kinetic energy of the stone decreases as much as potential energy increases. When we throw down the stone from the roof of the house, it will accelerate with decreasing height. This is a result of the law of conservation of energy. This study is based on the assumption that the law of conservation of energy will take place in the motion of gas molecules. So when a molecule falls down in the gravitational field, it accelerates. When a molecule rises up, it retards.

To exclude quantum effects [7], we consider gas xenon. At room temperature, equation (1) is correct for xenon molecules.

$$\langle p \rangle \cdot d \gg \frac{\hbar}{2},$$
 (1),

where  $\langle p \rangle$  – average momentum of xenon molecules at room temperature d – diameter of xenon molecules that is equal to 4,4Å,  $\hbar/2$  – Heisenberg uncertainty.

Equation (1) shows that xenon molecules are classic objects with certain positions and velocities. So the laws of classic mechanics are applicable for the xenon molecules. It is important that Eq. (1) is not true for hydrogen molecules at room temperature. So we must take into consideration quantum effects when studying the behaviour of hydrogen molecules.

It is well known [8] that heat and temperature are determined by molecular motion intensity. For example, the heat energy of monatomic gas is the total kinetic energy of the linear motion of this gas. The temperature of a monatomic gas [9] is determined by the average energy of linear motion of molecules of this gas by equation (2). So if a metal plate is placed into the gas, the gas molecules attack this plate with average energy from equation (2), where T – temperature of the gas. It is well known [9] that if the temperature of the plate is higher than that of the gas heat energy flows from plate to gas. If the temperature of the plate is lower than that of the gas heat flow from gas to plate. So if gas molecules attack a plate with average energy higher than  $\langle E_k \rangle$  from equation (2) where T – temperature of plate, heat energy will flow from gas to plate. This means that the average energy of gas molecules before interaction with the plate is higher than that after interaction with the plate.

$$\langle E_k \rangle = \frac{3}{2}kT, \tag{2},$$

where  $\langle E_k \rangle$  – average kinetic energy of gas molecules, *k* – Boltzmann constant, *T* – gas temperature.

It is important that the surface of the plate doesn't "know" the temperature of the surrounding gas. Plate "knows" only energies with which gas molecules attack this plate. It is established in [10] that angles of attack do not play any role also. So when a meteorite moves through a rarified atmosphere [11], it is heated to high temperatures by cold rarified gas. Meteorite surface accepts fast directed motion of molecules of cold gas exactly like chaotic heat motion of very hot gas.

Let's consider two infinite horizontal parallel metal plates and rarified gas xenon between them (see Fig. 1). All the system placed into zero gravity. As far as gas xenon is rarified gas molecules does not interact one with another [12]. They interact only with plates. After interaction with the top plate, gas molecule always interact with the bottom plate. After interaction with the bottom plate, the gas molecule interacts with the top plate again. For zero energy exchange between gas and top or bottom plate, it is necessary for the average energy of gas molecules before an interaction to be equal  $\langle E_k \rangle$  from equation (2) where T – temperature of the plate. In this case, the average energy of molecules after interaction will be equal to average energy of these molecules before interaction. In zero gravity average energy of molecules after interaction with the top plate is equal to the average energy of these molecules before interaction. In zero heat exchange, the average energies of molecules before and after interactions with top and bottom plates must be equal. So temperatures of the plates must be equal for the absence of heat exchange. It is well known (6) that this conclusion is correct.



Fig. 1. Xenon molecules between two horizontal metal plates

Now let's consider the system showed in Fig. 1 placed into strong gravity. For zero energy exchange between gas and top or bottom plate, it is necessary for the average energy of gas molecules before an interaction to be equal  $\langle E_k \rangle$  from equation (2) where T – temperature of the plate. The average energy of molecules after interaction with any plate is equal to the average energy of these molecules before interaction. When molecules moves from the top plate to the bottom plate, their average kinetic energy increase by potential energy. When molecules move from the bottom plate to the top plate, their average kinetic energy decrease by potential energy. This means that for zero heat exchange the temperature of the bottom plate must be higher than the temperature of the top plate by  $\Delta T_{gs}$  from equation (3).

$$\Delta T_{gs} = \frac{2mgh}{3k},\tag{3}$$

where *m* – the mass of xenon molecule, that is equal to  $2,2 \cdot 10^{-25}$  kg,

h – distance between plate, m,

g – gravity, m/s<sup>2</sup>,

k – Boltzmann constant, that is equal to 1,38 · 10<sup>-23</sup> J/K,

 $\Delta T_{gs}$  – temperature difference between plates.

The mechanism of heat transfer provided by motion and interaction of molecules is heat conductivity [8]. Thus  $\Delta T_{gs}$  is a gravitational shift of thermal equilibrium for the heat conductivity mechanism.

The most extraordinary feature of gravitational shift is that the equilibrium state is when temperatures of plates are different. In most common processes, the equilibrium state [13] is when all parts of the system have the same temperature.

# **RESULTS OF NUMERICAL SIMULATION OF MOLECULAR MOTION**

In our modelling [14], a simplified numerical model was used. The amount of molecules was 10 000 in modelling without interactions between molecules and 500 in modelling with interactions between molecules. It is much less than in reality. To achieve an effect of real gas, an effective diameter of molecules in the calculation was much bigger than in reality.

Interaction of molecules of monatomic gas was calculated as the collision of two spherical balls. The interaction of gas molecules with metal plate was calculated according to supposing that gas obtains temperature of plate T. This means that average energy of molecules after interaction with plate equals to  $\langle E_k \rangle$  from equation (2), where T – temperature of the plate. This simplification is reasonable because the heat capacity and heat conductivity of gas is much less than that of the metal plate [15]. As far as the real distribution of angles and energies of molecules after the interaction is unknown, all energies were accepted to be  $\langle E_k \rangle$ , and angles were accepted to have uniform distribution [0..180°).

Initial positions of molecules were established to have a uniform distribution in all the volume. Initial directions of motion were established to have a uniform distribution of angles  $[0..360^{\circ})$ . Initial speeds of molecules were established to have approximate Maxwell distribution by equation (4). In modelling, the rarified gas diameter of molecules was established as not very large for molecules to interact one with other very seldom.

$$V = 0.798 < V > \sqrt{-2\ln(Rnd)},$$
(4)

where  $\langle V \rangle$  - the average speed of molecules,

*Rnd* – random value having uniform distribution (0..1).

The numerical task showed in Fig. 1 was solved by numerical simulation of molecular motion. The results of numerical simulation are in good accordance with equations (3) and (5) obtained by theoretical analysis.

$$Q = \frac{\lambda \cdot \left(T_t + \Delta T_{gs} - T_b\right)}{h},\tag{5}$$

where Q – conductive heat flux per square meter,

 $\lambda$  – heat conductivity of the gas,

 $T_t$  – temperature of the top plate,

 $T_b$  – temperature of the bottom plate,

h – distance between plates.

For normal gas modelling, the molecular diameter was established large enough for molecules to interact one with another many times between interactions with plates. The gas is normal when the mean free pass of its molecules is much less than the distance between plates, but it is much greater than the diameter of the gas molecule [16]. The growth of thermal energy of the bottom plate for rarified gas was compared with that for normal gas. The numerical simulation does not show a significant difference between normal and rarified gas.

May be chaotic motion and interaction of gas molecules can not eliminate an effect of gravitational shift because of two factors. The first factor is that rising molecules always slow down, and falling molecules always speed up despite the direction of motion. The second factor is that when molecules interact one with another, their average kinetic energy remains the same.

When the top is colder than the bottom, the convection always appears in normal gas [17]. This convection did not appear in simulation because the number of molecules in modelling was much less than that in real life. So convection process was analysed only theoretically. Somebody can say that this convection immediately equalizes temperatures, but it is not so. At strong gravity, the gas layer creates high hydrostatic pressure. So rising gas always expands and cools, and falling gas always compresses and heats. Thus convection in strong gravity creates a temperature difference:

$$\Delta T_{sc} = \frac{2mgh}{(i+2)k},\tag{6},$$

where i – number of degrees of freedom of molecular motion.

This convection appears only when the temperature difference in gas is higher than  $\Delta T_{sc}$ . So  $\Delta T_{sc}$  is a resulting temperature difference in normal gas placed into a strong gravitational field.

Numerical simulation of molecular motion was made for monatomic gas. Effects in polyatomic gas were analysed theoretically. It was established that the shift of thermal equilibrium for polyatomic could be calculated by equation (7).

$$\Delta T_{gs} = \frac{2mgh}{ik} \,. \tag{7}.$$

The total energy that molecules give to the bottom plate was calculated during the numerical simulation process. It was shown that when temperatures of plates are equal, heat flux Q per square meter is:

$$Q \propto m^{\frac{1}{3}}$$
 (8).

Looking at Eq. (7), we understand that the temperature difference of gravitational shift  $\Delta T_{gs}$  is maximal for heavy monatomic gases. Equation (8) shows that heat power of heat conductivity caused by the gravitational shift of thermal equilibrium is maximal for heavy gases. Thus, xenon is the most appropriate gas for our studies.

To understand molecular behaviour in artificial gravity created by centrifuge, the 2D circular task was solved (Fig. 2).



Fig. 2. Cross section of the gas centrifuge

A gas is placed between the shaft and shell of the centrifuge. Shaft and shell rotate with the equal angular speed. The diameter of the centrifuge is 50 mm, and the height of the gas layer is 6 mm. The length of centrifuge is equal to 300 mm. The average speed of molecules is 200 m/s. The circular speed of the centrifuge is also equal to 200 m/s. This circular speed is maximal which may be achieved by metal centrifuge [18].

During the modelling of the circular task showed in Fig. 2, a simplification was used. As far as the distance between shaft and shell is much less than centrifuge diameter circular task was replaced by a rectangular task where the top plate is a shaft and the bottom plate is a shell. In modelling, Coriolis force [19] was taken into account as far as centrifugal gravitation. All these forces are shown in equation (9).

$$\begin{cases} g = \frac{V_c^2}{R} \\ a_x = \frac{2gV_y}{V_c} \\ a_y = \frac{-2gV_x}{V_c} \end{cases}, \tag{10},$$

where g – centrifugal gravity,

 $V_x$  – horizontal (circular) speed of molecule,

 $V_y$  – vertical (radial) speed of molecule,

 $a_x$  – acceleration by horizontal Coriolis force,

 $a_y$  – acceleration by vertical Coriolis force,

 $V_c$  – circular speed of the centrifuge.

Numerical simulation of molecular motion in centrifuge did not show any difference in increasing of thermal energy of bottom plate in comparison with natural gravity. So we can say that centrifuge can be used to create a gravitational shift of thermal equilibrium for heat conductivity mechanism in gas.

#### Technical realization of the method

For the realization of the method of conversion heat to electricity using the thermal shift effect, it is necessary to create gravity 100 000 times higher than that of the Earth [14]. Such high gravity is necessary for the effect to appear in a thin gas layer where heat conductivity is stronger than radiative heat transfer [20]. Besides heat conductivity of construction must be less strong than the heat conductivity of the gas. A schematic view of the engine in a cross section is showed in Fig. 3.



Fig. 3. Schematic section of molecular action heat engine without background

A centrifuge is the main part of the engine. It creates a necessary gravity in which temperature difference appears due to the effect of gravitational shift. The centrifuge consists of shaft, flanges and shell. A space between shaft and shell is fulfilled by xenon in which a gravitational shift takes place. An external surface of the shaft and the internal surface of the shell is polished for blackness being minimal. It is necessary to minimize a radiation heat exchange between shaft and shell. Flanges are very thin and made from plastic with low heat conductivity. It is necessary to minimize conductive heat exchange between shaft and shell. This heat exchange as soon as radiative heat exchange reduces an effect of gravitational shift. The external surface of the shell and internal surface of the radiative heat keeper is black to maximize a radiation heat transfer.

When the centrifuge rotates, a gravitational shift of thermal equilibrium appears in xenon. This shift creates a temperature difference between the shaft of centrifuge and its shell. The radiative heat keeper and radiative heat exchanger are used to take off a temperature difference from a rotating centrifuge without mechanical contact with it. Mechanical contact with static parts is inadmissible for the centrifuge to rotate without friction. The radiative heat exchanger and radiative heat keeper take off a temperature difference from the centrifuge and gives this difference to thermoelectric converter [3]. The thermoelectric converter converts temperature difference to electricity.

When some part of heat energy being converted to electricity in a thermoelectric converter, all the system became colder. To avoid overcooling, the setup is equipped with a heat supply. Heat supply gives heat to the system from the outside.

A centrifuge is established on special suspension. This suspension consists of eight trundles, only four of which are illustrated in Fig.3. A suspension is necessary for the centrifuge to rotate quickly with minimal friction. To avoid viscous friction, all the system is placed into high vacuum  $\sim 10^{-6}$  Pa. Vacuum also needs to diminish parasite heat transfer.

If suspension would ideal and a vacuum would absolute, an electric motor will be unnecessary. According to the law of conservation of angular momentum, the centrifuge must rotate perpetually after being once started. It is because the centrifuge is an enclosed system. Gas in centrifuge is unmovable in respect to centrifuge. This is the main difference from vortex tube when gas pass through the system continuously and we must constantly spend energy for giving rotation to the gas. In this system gas does not pass through the centrifuge. Being once accelerated it rotates all the time. The source of energy is not electric motor but heat from outside. So electric motor is necessary only for compensation of friction. In reality, friction caused by suspension and vacuum must take less energy than the thermoelectric converter generates. This challenge compels us to make a high quality suspension, well balanced centrifuge and high vacuum.

#### CONCLUSIONS

The heat transfer in gases placed into strong gravitation is not the same as in Earth gravity. The gravitational shift of thermal equilibrium for heat conductivity appears only when gravity is very high.

An effect of the gravitational shift of thermal equilibrium for heat conductivity takes place in different gases. Convection effects appear only in normal gases. The temperature difference of heat conductivity gravitational shift is always higher than the temperature difference created by convection.

Temperature difference caused by gravitational shift for heat conductivity is maximal for heavy monatomic gases. The heat flux caused by gravitational shift for heat conductivity is maximal for heavy gases. Xenon is the most appropriate gas for the conversion of heat to electricity via molecular action.

The gravitational shift of thermal equilibrium for heat conductivity appears in a centrifuge as far as in natural gravity. The growth of thermal energy of the bottom plate in natural gravity is the same as in centrifugal gravity of the same magnitude.

Conversion heat to electricity via molecular action on the gas seems to be technically possible. The main difficulties are high vacuum, high speed and well balanced centrifuge, low friction suspension and good radiative isolation.

This study is based on numerous assumptions and simplifications. The real mechanism of molecular motion and interactions is not clear enough to rely on some numerical estimations. Thus, experimental verification of all the results is necessary.

Probably somewhen molecular action heat engine became a good alternative for common heat engines of thermodynamic action.

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# METHODOLOGICAL APPROACH TO SOLVING ENERGY SAVING ISSUE BASED ON THE USE OF SECONDARY ENERGY RESOURCES

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#### ABSTRACT

The possible sources of primary energy for generating heat and electricity are analyzed. It's shown that the preference will be given to renewable and secondary energy resources (SER) when generating electricity. The analysis of literature sources showed that there is no single approach to assessment the potential and possible solutions at the SER utilization. The attention is paid at the creation of a hierarchical structure of methodological approach for solving the issues of energy saving at facilities which include SER (thermal, fuel, overpressure) in the work. This will allow to get a consistently and complexly approach to improving the efficiency of fuel resources using. The global issue of SER utilization is solved in the general case. At each stage a search for a local rational solution is carried out. The methodology construction is based on the use of Pareto set and on the expert information about the relative importance of criteria. All this makes it possible at each stage to determine a rational solution to the issue of energy saving on the basis of existing energy efficient technical solutions implementation, one of which is steam turbine cycles on low-boiling working fluids (LBWF).

The main periods of methodological approach are: the determination of the type and energy potential of SER at the facility; the conversion priority of SER into cold, electrical and thermal energy; the selection of a thermal scheme and the LBWF; the estimate of the cycle thermodynamic efficiency; the technical and economic estimate of the obtained version of SER utilization; the selection and/or design and manufacture of the necessary equipment for the thermal schemes.

It is proposed to choose heat exchange equipment from those available in the petrochemical industry which will allows to reduce the design costs. The turbine implementation, in most cases, requires an individual approach and design for each energy saving solution. The hierarchical structure of methodological approach will allow a complex approach to solving the issue of energy saving at the SER utilization.

As an example, studies of a energy installation are presented, which allowed the characteristics of the thermal scheme is obtained, rational variants of heat exchange equipment are proposed.

**Keywords**: secondary energy resources, rational solution, hierarchical structure, energy saving, electricity, turbine cycle, low-boiling working fluid

#### **INTRODUCTION**

Currently, more and more attention is paid at solving the issues of energy saving in various economy sectors to improve the efficiency of the fuel and energy resources used.

By the end of the last century, in the production of electricity preference was given to oil, natural gas and coal. At the beginning of the XXI century, the energy resources redistribution is carried out in the direction of renewables and secondary energy resources (SER).

According to their energy potential and the way of using them, SER are divided into combustible, thermal and overpressure [1, 2].

The use of SER can be varied and allows you to get:

- electricity;

- thermal energy for domestic hot water (DHW), heating and technological needs;

- cold for air conditioning, food storage, etc.
A modern perspective direction for solving the issue of using SER is the implementation of turbine cycles on low-boiling working fluids (LBWF) [3-7]. Thus, condensation, cogeneration and trigeneration cycles are realized. Heat exchange equipment, heat pump and refrigeration cycles are used for the production of warm energy and cold [8].

In the modern scientific literature the expediency of various thermodynamic cycles realization at SER utilization is fragmented, however to creation of the methodological approach for the decision of energy saving issue is not enough attention [3-8]. Based on this, the methodological approach creature to solve the issue of the useful SER use is very interest. This will make it possible to rationally approach the set task both at the stage of creating a new power plant, and when improving an existing facility, which has a sufficient potential for SER.

The work is devoted to the presentation of a methodological approach to the energy saving measures implementation based at the SER utilization in the production of cold, heat and electricity. The main stages of the search for a rational solution are outlined.

#### GENERALIZED METHODOLOGICAL APPROACH TO SER UTILIZATION

Based on the analysis of literature sources and our own scientific research, a generalization of existing approaches to solving the energy saving issues at the SER utilization (heat, fuel and overpressure) has been made. A hierarchical structure of methodological approach to solving this problem has been built and proposed, which includes a certain sequence of analysis and calculation of existing objects, selection and recommendations for the implementation of possible energy saving technical solutions. This structure is shown in Fig. 1, Fig. 2.

Methodological approach summarizes the existing and developed by the authors mathematical models and methods for creating energy saving technologies by using various thermodynamic cycles relative to various sectors of the economy. According to the given structure, an appropriate sequence of calculation researches is carried out in order to determine the feasibility of introducing energy saving measures and the weight, size and gas-dynamic characteristics of the thermal scheme elements.

The global aim is to solve the problem of energy saving at the SER utilization. This aim is achieved by carrying out a certain sequence of analytical and computational research. The main stages of the methodological approach are:

- determination of the type and energy potential of SER at the facility (combustible, thermal and overpressure);

- establishment the priority of the conversion of SER into cold, electric and thermal energy;

- the choice of a variant of the thermal scheme and a working fluid;

- calculation of the cycle thermodynamic efficiency;

- project feasibility study of SER utilization;

- selection and/or design and manufacture of the necessary equipment for the thermal scheme.

At each stage, the problem of finding a local aim is solved, that is, a rational solution based on the existing Pareto method, which is widely used in various industries [9-11]. This allows, using a well-known approach, to determine the feasibility of introducing energy saving measures and to determine weight, size and thermo-gas-dynamic characteristics of the elements. It enables to be attached to the existing working conditions of the research object.



Fig. 1. The hierarchical structure of the upper level of methodological approach to the construction and calculation of thermal schemes and their main elements : STU – steam turbine unit; UTEU – utilization turbo expander unit; GTU – gas turbine unit; GPE – gas piston engine; RU – refrigeration unit; HPU – heat pump unit; DWHRS – deep waste heat recovery system; HEE – heat exchange equipment; ACS – air climate system



Fig. 2. The hierarchical structure of the lower level of methodological approach to the construction and calculation of thermal schemes and their main elements

For each stage of the search for a global aim, it is relevant to determine a specific aim of the corresponding stage. A characteristic feature of each stage is a certain finite set of possible solutions *X*, from which a rational solution must be chosen. In a broad sense, a rational solution is considered to be such a solution that most fully satisfies the global aim (from the point of view of the given conditions and the available potential of SER).

At forming a mathematical model of decision making, the degree of satisfaction of the specified aim is expressed using one numerical criterion f in such a way that a greater value of this criterion corresponds to a greater degree of aim achievement, and a lesser one – to a lesser extent. In this case, the question of choosing a rational solution is reduced to the usual (one-criterion) problem of maximizing a numerical function (criterion of the first level) f on the set of possible solutions X and the solution of this problem does not cause fundamental difficulties [12].

Denoting i – the number of a possible solution (sub-aim) at a certain stage of the search for the global aim  $f_i$ . If the *i*-th sub-aim requires additional partitioning into a number of even simpler sub-aims of the next level and try to construct a corresponding set of third level criteria  $f_{i1}, f_{i2}, ..., f_{im}$  for their mathematical expression. In this way, as a result of performing a certain finite number of described actions, a hierarchical structure of aims is built (Fig. 1, Fig. 2).

At solving the issue of energy saving on the basis of SER utilization, a multicriteria problem with a complex hierarchical structure of aims  $f_n$  with a set of possible solutions at the

appropriate stages is solved. At each stage of decision-making, it is important to analyze and consider the expert's comparison of the set importance of the corresponding hierarchical level  $f_1, f_2, ..., f_m$  criteria. In some cases, you need to keep in touch between the levels.

Denoting *n* is the number of possible solutions  $(X = \{x_1, x_2, ..., x_n\})$ . Each criterion  $f_a$  of the lower level in the hierarchical structure of aims must be matched by an *n*-dimensional vector of values  $(f_a(x_1), f_a(x_2), ..., f_a(x_n))$ . The first stage of the calculation is completed.

At the next stage, among the lower level criteria are groups that are subject to the same aim (criterion). For each such group with the involvement of experts using the method of hierarchy analysis, a vector is calculated, the components of which express the normalized weights for this group criteria in relation to the criterion under which they are subordinated. The dimension of the obtained normalized weight vector will be equal to the number of criteria of this group. Then the criterion, under which the criteria of this group are subordinated, is a vector representing a weighted sum of *n*-dimensional vectors that meet the criteria of this group and obtained in the first stage, and the coefficients of this sum are the components of the vector expressing the found normalized weights criteria [12].

It should be borne in mind that the search for a rational solution at each stage is accompanied by a number of restrictions on the design parameters of the power plant U, defining parameters Y (thermodynamic parameters and efficiency), given external factors Z (outside air temperature, etc.), a set of equations of balances for all elements of installation  $F_i$  [13].

The given hierarchical structure and conditions of the decision of problems of search of local purposes allow in directed way approaching the solution of energy saving issue at the SER utilization for production of cold, thermal and electric energy.

#### MAIN STAGES OF THE METHODOLOGICAL APPROACH

The main issues that are resolved with energy saving based on the utilization of SER for the purpose of generating heat and electric energy include:

1. Determining the type, energy potential of SER at the facility and possible technical solutions:

-<u>waste heat of technological processes</u> with temperature 80–350 °C (does not depend on the season);

-<u>flue gases of municipal energy facilities</u> with temperature 80–200 °C (depends on the season);

- geothermal energy sources with temperature 100-250 °C;

- <u>combustion of renewable fuel resources</u> with temperature 300–500 °C (depends on the region of location and purpose of implementation);

-<u>overpressure of technological processes</u> in the gas transmission system, chemical and other sectors of the economy.

- 2. **Possible technical solutions for the introduction of power generating equipment** (steam turbines, gas turbines, gas piston engines, utilization turboexpander units, refrigeration units, heat pump units, deep heat utilization systems, heat exchange equipment).
- 3. Establishing of SER conversion priority into electric energy, thermal energy and cold (weight coefficients  $K_{Ee}$ ,  $K_H$ ,  $K_C$ ):
  - -<u>weight coefficient</u>  $K_{Ee}$  (the importance of obtaining electricity from SER);
  - -<u>weight coefficient</u>  $K_H$  (the importance of obtaining thermal energy from SER);
  - -<u>weight coefficient</u>  $K_C$  (the importance of getting cold from SER).

The sum of the coefficients must be equal to one  $(K_E + K_H + K_C = 0)$ .

4. Selection (refinement) of a typical version of the scheme and the working fluid of the thermal cycle and evaluation of its thermodynamic efficiency (weight coefficients  $K_{te}$ ,  $K_{ecol}$ ,  $K_{cost}$ ):

-<u>use of different variants of thermal energy cycles</u> (for example, Fig. 3, Fig. 4) and conducting their analysis in order to assess their thermodynamic efficiency and determine the coefficient  $K_{te}$ :

$$K_{te(i)} = (N_E + N_H + N_C)_i / (N_C + N_H + N_C)_{max}; \quad (1)$$





Fig. 3. Dual-contour cogeneration unit: 1 – evaporator; 2 – turbine; 3 – electric generator; 4 – condenser; 5 – feed pump;
6 – regenerative heat exchanger; 7 – heat exchanger-cooler; 8 – throttle device; 9 – cooler; 10 – compressor [14] Fig. 4. Thermal scheme with heat recovery and intermediate heating medium: 1 – gas-oil heat exchanger; 2 – circulating pump; 3 – evaporator;

4 – turbine; 5 – electric generator; 6 – recuperator; 7 – condenser; 8 – feed pump [2]

- assessment of environmental weighting factors  $K_{ecol}$  and  $\underline{cost} K_{cost}$  LBWF:

$$K_{ecol(i)} = E_{k(i)}/E_{k(max)}, \quad K_{cost(i)} = B_i/B_{max}.$$
 (2)

The expediency of using low-boiling working fluids in thermodynamic cycles is regulated by weighting factors (the higher  $K_n$ , the more significant its influence in the formation of the power plant):

<ul> <li><u>- thermodynamic</u> (K<sub>4</sub>):</li> <li>appropriate boiling point;</li> <li>condensation pressure above atmospheric;</li> <li>high thermal conductivity;</li> <li>low viscosity LBWF.</li> </ul>	<u>– economic</u> (K <sub>2</sub> ): – availability of commodity production; – affordable (low) price.
<u>– ecological</u> (K <sub>3</sub> ): – ozone safety; – low global warming potential.	<ul> <li><u>- operational</u> (K<sub>1</sub>):</li> <li>- thermochemical stability;</li> <li>- chemical compatibility with materials;</li> <li>- incombustibility;</li> <li>- explosion safety, etc.</li> </ul>

The distribution of the weight of the coefficients is based on the expert assessment of a specialist;

- <u>thermal schemes modelling</u> (the initial data for the thermal scheme are the parameters of the SER source and the thermodynamic properties of the working fluids). The processes in the elements and connections of the installation are described by the following equations:

– energy balance equation for each *k*-th element of the scheme:

$$\sum_{j=1}^{J_k - K_k} (\eta \cdot G \cdot h)_j + \sum_{j=1}^{K_k} (\eta \cdot E)_j = 0,$$
(3)

– balance equations of costs for each l-th energy carrier of the k-th element of the scheme:

$$\sum_{j=1}^{J_{kl}} G_j = 0, (4)$$

– equation of the hydraulic balance of costs for each l-th energy carrier of the k-th element of the scheme:

$$(p_{in} - \Delta p - p_{out})_{kl} = 0, \tag{5}$$

- equation of enthalpy change for each *l*-th energy carrier of the *k*-th element of the scheme:

$$(h_{in} - \Delta h - h_{out})_{kl} = 0, \tag{6}$$

- total electricity production during the year:

$$N_{season} = \sum_{i=1}^{n} N_i \cdot \tau_i. \tag{7}$$

#### 5. Feasibility study of the resulting version of SER utilization:

- <u>possible production of energy of the highest quality</u> in the utilization installation at the expense of SER:

– heat in the form of hot water:

$$Q_H = G_{SER} \cdot \left( c_{p1} \cdot t_1 - c_{p2} \cdot t_2 \right) \cdot k_{cost \, H} \cdot \tau_{year} \cdot \eta_{u \, u}, \quad (8)$$

- electricity:

$$N_E = G_{SER} \cdot \left( c_{p1} \cdot t_1 - c_{p2} \cdot t_2 \right) \cdot k_{cost E} \cdot \tau_{year} \cdot \eta_{u u} \cdot \eta_m \cdot \eta_g,$$
(9)

- cold:

$$Q_C = Q_H \cdot \varepsilon, \tag{10}$$

- payback period of the project:

$$\tau_{pbp} = \frac{k_T + k_E + k_C}{Profit},\tag{11}$$

where  $k_T$ ,  $k_E$ ,  $k_C$  – capital investments in heat, electricity and refrigeration units; *Profit* – enterprise profit from reconstruction and modernization;

- <u>economic effect</u> of the SER use is determined by the difference in the annual costs of comparative options:

$$E = C_{w \, use} - C_{use} - E_n \cdot (k_{use} - k_{w \, use}), \qquad (12)$$

where  $C_{w use}$  – annual operating costs without the use of SER;  $C_{use}$  – annual operating costs using SER;  $E_n$  – normative efficiency ratio of capital investments;  $k_{use}$  – capital investments required for project implementation using SER;  $k_{w use}$  – capital investments required for project implementation using SER;  $k_{w use}$  – capital investments required for project implementation set.

6. Selection and/or design and manufacture of the necessary equipment of the thermal scheme elements (weight coefficients  $K_{ef}$ ,  $K_{ws}$ ,  $K_{cost}$ ):

- <u>the choice of thermal scheme equipment from the market</u>, which will reduce the cost of designing a new one;

- <u>use of existing approaches to the formation and calculation</u> of turbines flow parts and heat exchange equipment and their analysis in order to assess their efficiency and determine the coefficient  $K_{ef}$ :

$$K_{ef(i)} = N_{E(i)}/N_{E(max)},\tag{13}$$

- assessment of mass and size and cost weight coefficients of equipment  $K_{ws}$ ,  $K_{cost}$ :

$$K_{ws(i)} = M_{ws(i)}/M_{ws(max)}, K_{cost(i)} = C_{cost(i)}/C_{cost(max)}.$$
 (14)

Carrying out of settlement researches on definition of characteristics of heat exchangers on various working fluids is based on the developed software product. It allows to estimate the overall dimensions of the heat exchange equipment which is a part of the thermal scheme and to select it from existing (developed) types of heat exchangers of the oil and gas industry. This solution makes it possible to reduce the production time and cost of designing new heat exchangers. National standards and technical conditions of manufacturers are taken as a base.

Calculations of heat exchange equipment are based on generally accepted equations. Based on the results of the calculation, the analysis of the heat exchanger design is performed and, if necessary, the geometric characteristics of the heat exchange equipment are reviewed, after which the calculation is performed again. From several variants of heat exchangers the best variant which satisfies both on the size of hydraulic resistance, and on mass-dimensional parameters is chosen. In the absence of a heat exchanger suitable for consumption and thermal characteristics, there is a need to design a new heat exchanger. According to the results of choosing a rational design, the mass and size characteristics of the heat exchanger are determined.

As a result of the conducted scientific researches the hierarchical structure of the multicriteria approach for the decision of energy saving issue at the SER utilization is constructed and offered (Fig. 1, Fig. 2). The complex approach will allow a rational walk up to the task, taking into account possible technical solutions and relationships between the relevant stages of solving the problem of energy saving.

#### AN EXAMPLE OF USING THE METHODOLOGICAL APPROACH

For an example of using a methodological approach, a variant of improving a cogeneration bioenergy installation is presented. A bioenergetic installation with a working fluid MDM developed by the Szewalski Institute of Fluid-Flow Machinery PAS is the object of research [15]. The installation operates only in winter in cogeneration mode. A variant of improving the cogeneration unit by using the second cascade and changing the MDM parameters at the outlet of the turbine to condense it at a pressure close to atmospheric is proposed. Particular aspects of solving this problem were considered in [13, 18]. At working fluid choosing for a turbine cycle, it is necessary to take into account the demands (noted earlier). At working fluid choosing for the second cascade, a number of LBWF were reviewed.

Taking into account the working fluid properties chosen for realization in the second cascade, and the characteristics of the first cascade working fluid, the thermal scheme of two-cascade power plant is proposed (Fig. 5). The initial steam parameters of the second cascade were selected according to the temperature of the steam at the outlet of the turbine of the first cascade. The actual process of steam expansion in the turbine should end near the boundary dryness curve. The analysis showed that R-600a is rational working fluid for the second cascade [2]. The parameters of the working fluid at the control points of the thermal scheme are presented in Fig. 5.



Fig. 5. Two-cascade energy installation: I – first contour (intermediate); II – second contour (electricity generating); III – third contour (heat supply and DHW); IV – fourth contour (electricity generating); V – fifth contour (working fluid condensation system); 1 – circulation pump; 2 – boiler unit; 3 – evaporator; 4, 12 – turbine; 5, 13 – electric generator; 6 – recuperator; 7 – boiler installation; 8 – network pump; 9, 15 – feed pump; 10, 11 – evaporator and heater LBWF of the second contour; 14 – condenser; 16 – circulation pump of cooling system

Local fuel (LF) is used as VER. The cost indicators of LF different types are discussed in [18]. For the energy installation, the prices of equivalent fuel are  $c_{e.f.}$  40, 60, 80 USD/t. The electric power of the two-cascade energy installation is 100 kW. The biofuel boiler efficiency ( $\eta_b = 0.85$ ) and the thermal power supplied to the 1st cascade ( $Q_b = 500$  kW) are constant throughout the year. Equivalent fuel consumption per hour  $b_{e.f.} = 72.21$  kg/h [2]. The equipment utilization factor is  $k_u = 0.95$ , the average length of the month is  $\tau_{month} = 730$  hours, the monthly fuel costs are  $C_{month} = 50 \cdot c_{e.f.}$ , (USD/month). The monthly salary of the maintenance personnel (12 people) of the energy installation is 4800 USD (for Ukraine). Fuel and personnel costs account for 90% of all monthly maintenance costs of the energy installation [2].

The energy installation operation during the year is considered as the average values of the length of the year and the day for Ukraine. At the  $c_{\text{e.f.}} = 40 \text{ USD/t}$  [18] the cost of electricity in cogeneration operation modes of the energy installation  $0.028 - 0.072 \text{ USD/(kW} \cdot h)$ . The cost price of electricity generation in the summer at night (without DHW) increases to  $0.146 \text{ USD/(kW} \cdot h)$ . During the heating period, the cost price of the heat energy supply is competitive. The cost price of DHW in summer is 84.3 USD/Gcal. At the given conditions, the simple payback period of the energy installation is 2.2 years.

The influence of the energy carriers cost on the payback period of the energy installation with 100 kW electric power is shown in Fig. 6.



At a price of 2000 USD/kW, the implementation of the energy installation with 100 kW electric capacity is promising in a wide range of prices for equivalent fuel is shown in Fig. 6. The availability of a heat consumer has a significant influence on lowering the payback period of the energy installation. The energy installation exploitation only pure condensing mode operation will not be cost effective.

After assessing of expediency of the project, we move on to the second hierarchical level – the selection and calculation of the thermal scheme main elements.

As said earlier, heat exchangers are selected from those available in the petrochemical industry. The choice is carried out using the developed design model. Calculation studies have shown that the total mass of the heat exchange equipment is  $\sim 12$  tons [4].

The turbine is designed individually for each case. The calculation of the flow path of a turbine with a working fluid MDM is presented in [16, 17]. The calculation of the flow path of the turbine with R-600a was carried out for define it rational design. The initial data are taken from Fig. 5. The type of turbine (axial and radial-axial) and the number of stages were varied. It was found that it is expedient to implement a two-stage turbine of the radial-axial type. For an axial turbine, the number of stages will be 7. This will lead to an increase in weight and size characteristics in comparison with a radial-axial turbine [2].

#### CONCLUSIONS

The methodological approach to rational decision-making in the construction, calculation and research of possible technical solutions for the rational use of SER is proposed. This approach will allow a complex and structured approach to solving the issue of energy saving, taking into account the characteristics of SER sources (heat, fuel, overpressure) in order to generate cold, heat and electricity and assess their economic and technical feasibility. The proposed methodology allows determining the characteristics of the main heat flows, on their basis choosing the main and auxiliary equipment, its consumable and mass characteristics.

Studies have shown that the task of finding a rational solution is multi-criteria and multistep. At the solving the energy saving issue in the utilization of SER, the global aim includes many local aims. The search for each local aim is carried out by using modelling and expert assessment of the specialist based on his experience.

Studies of the cogeneration power plant realization feasibility have shown that for the variant was proposed; it is rational to choose the heat exchange equipment available in the petrochemical industry, the total weight of which will be ~12 tons. As a result of calculations, a 2-stage radial-axial turbine with electric power of 73 kW with a relative internal efficiency of 80 % was obtained. The payback period will vary from 2.2 to 4.2 years depending on the energy carriers cost.

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# SHORT-TERM NONINDUSTRIAL REACTIVE POWER FORECASTING

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#### ABSTRACT

In recent years, energy forecasting applications not only on the grid side of electric power systems but also on the customer side for load and demand prediction purposes have become crucial after becoming widespread of distributed generation and advancements in the smart grid technologies. As one of the energy forecasting applications, reactive power forecasting plays a significant role in energy management and planning of industrial and nonindustrial facilities supplied by the distribution network. Hospitals may be described as highly sophisticated organisations because of the fact that the reliability of uninterrupted energy flow has utmost importance owing to their continuous duty for 24/7 operation without any excuses. Short-term reactive power forecasting is an essential tool that is not merely required for ensuring voltage stability but also satisfies the demand by monitoring reactive power consumption, finds base and peak demands, minimises risks by reducing power outages, makes viable decisions in regard to maintenance planning and further investments. In this paper, research and implementation of real-time short-term reactive power forecasting using machine learning algorithms including gradient boosted decision trees, group method of data handling polynomial neural networks, and support vector machines, have been carried out for a large hospital complex located in Adana, Turkey. To the best of our knowledge, there is a gap in the literature for real-time applications of reactive power forecasting and this paper is considered to fill the gap along with assisting prospective researchers in the field.

Keywords: Reactive Power Forecasting, Short-Term, Machine Learning, Building, Hospital

#### **INTRODUCTION**

Along with the latest developments in microgrids and smart grids, electric load forecasting has increased its importance because of the fact that it redresses a delicate balance among distributed generation and consumption of electricity for all sort of buildings.

Hospitals can be considered as complex organisations from a variety of views and uninterrupted energy flow has utmost importance because of their continuous operation. Shortterm reactive power forecasting is a crucial tool for all facilities in order to ensure voltage stability, monitor reactive power consumption, find base and peak demands, minimise risks via reducing outages, and make viable decisions related to maintenance planning and forthcoming investments.

Owing to the nonlinear characteristics of electric loads, machine learning algorithms are often used in reactive power forecasting. In the reactive power forecasting literature, Pu and Chen used artificial neural networks (ANN) with backpropagation for one hour-ahead and dayahead substation reactive power forecasting [1]. Cho et al. utilised the relationship between real and reactive power for an hour-ahead reactive power forecasting based on the ordinary least squares method [2]. Fidalgo and Lopes performed ANN with adaptive backpropagation to predict an hour-ahead and day-ahead active and reactive power at substation transformers [3]. Mu et al. employed a hybrid algorithm composed of quadratic self-adaptive exponential smoothing and converse exponential model for two different buses in a substation of a large iron and steel enterprise [4]. Akbulut and Gül emphasised the importance of reactive power in electricity markets by forecasting the reactive power of İstanbul's European part between 2011 and 2015 with the help of the least mean squares method [5]. Arruda et al. suggested an ANN-based topology to predict disaggregated active and reactive power at substation transformers [6]. Zhang et al. forecasted short-term active and reactive powers in a small district with nonlinear autoregressive neural networks [7]. Kaloudas and Shaw develop an approach to predict reactive power demand in distribution systems [8]. Ugwudike and Madueme preferred adaptive neuro-fuzzy inference system to forecast reactive power in distribution transformers [9]. Junior et al. calculated very-short term bus reactive power in Brazil's electric power system via knowledge data discovery [10]. Bracale et al. investigated probabilistic forecasting of active and reactive power in the industry with quantile regression forests and vector autoregressive exogenous models [11]. Lastly, Bracale et al. applied multiple linear regression and support vector machines (SVM) for short-term reactive power forecasting of an Italian factory at both aggregate and individual loads [12].

In this paper, a research and implementation of real-time short-term reactive power forecasting using machine learning algorithms including gradient boosted decision trees (GBDT), group method of data handling polynomial neural networks (GMDH networks), and SVM for a large hospital complex has been carried out. To the best of our knowledge, there is a gap in the literature for real-time applications of reactive power forecasting and this paper is considered to fill the gap along with assisting prospective researchers in the field.

#### **MATERIAL AND METHODS**

The material and methods used in this paper are presented as follows.



Fig. 1. Summary of the data set and flowchart of the forecasting process

#### Material

The material of this paper is a data set with a resolution of 1-hour between 2 October 2017 and 1 October 2018. The data set belongs to a large hospital complex located in Adana, Turkey. Meteorological variables are acquired from MERRA-2 [13]. Linear interpolation

method is used for imputing the data set's missing values. Predictors and target of the data set and their categories are summarised in Fig. 1, and Fig. 2 illustrates reactive and real power.



Fig. 2. A demonstration of the reactive and real power

# Methods

In this paper, GBDT, GMDH networks, and SVM are employed as forecasting methods.

# **Gradient Boosted Decision Trees**

Boosting is a series approach for aggregating weighted outputs of several simple models recurrently to obtain an enhanced accuracy of prediction by minimising loss functions [14].



Fig. 3. An illustration of the GBDT algorithm

Gradient boosting employs additive models which are trained in a forward stage-wise manner of the form

$$F_m(x) = F_{m-1}(x) + h_m(x)$$
(1)

where  $h_m(x)$  are decision trees of constant size,  $F_m(x)$  is the summation of *m* decision trees, and *x* is the set of input variables. In order to predict the response  $Y_{i,t+k}$  from the training set for the best  $h_m$ 

$$F_m(x_{i,t}) = F_{m-1}(x_{i,t}) + h_m(x_{i,t}) = Y_{i,t+k}$$
<sup>(2)</sup>

which yields to

$$h_m(x_{i,t}) = Y_{i,t+k} - F_{m-1}(x_{i,t})$$
(3)

where  $h_m$  also corresponds to  $r_{m,i,t}$  which stands for the model fitting the current residuals at iteration m. Note that current residuals are the negative gradients of the squared error loss function

$$r_{m,i,t} = -\frac{\partial \frac{1}{2} \left( Y_{i,t+k} - F_{m-1}(x_{i,t}) \right)^2}{\partial F_{m-1}(x_{i,t})}$$
(4)

which also indicates that  $h_m$  equals to the negative gradient of the squared error loss function.

In GBDT, a learning rate v so called shrinkage factor is defined to scale the contribution of each decision tree for a regularisation strategy which is utilised to avoid overfitting, may be stated as

$$F_m(x) = F_{m-1}(x) + vh_m(x), \qquad v \in [0;1]$$
(5)

where small values of v is recommended for better test error [15].

In this paper, the GBDT algorithm is chosen as a forecasting method due to its ability for superior accuracy of prediction, being computationally fast and efficient, and being flexible for different loss functions [16].

#### Group Method of Data Handling Polynomial Neural Networks



Fig. 4. A demonstration of the GMDH modelling process

Fundamentally, GMDH networks run as self-organising networks to generate the best model for the highest accuracy without overfitting. Hence, GMDH networks traditionally perform the ordinary least squares method to find an optimal mathematical equation between predictors and target variable by a reference function as follows

$$y = a_0 + \sum_{i=1}^n a_i x_i + \sum_{i=1}^n \sum_{j=1}^n a_{ij} x_i x_j + \sum_{i=1}^n \sum_{j=1}^n \sum_{k=1}^n a_{ijk} x_i x_j x_k + \cdots$$
(6)

where y is the target variable,  $X = (x_1, x_2, ..., x_n)$  corresponds to the predictor vector, and a represents the coefficient [17].

Typically, Eq. 6 is employed in the quadratic form of two variables such that

$$y = a_0 + a_1 x_i + a_2 x_j + a_3 x_i x_j + a_4 x_i^2 + a_5 x_j^2$$
(7)

Assume that each predictor corresponds to a neuron labelled as x in the input layer. Neurons in the first layer obtain their inputs from two of the predictors in the input layer. The neurons in the following layers acquire their inputs from two of the neurons in the preceding layer and this progress carries on up to the output layer. Herein, it should be emphasised that one neuron may also bypass layers directly from the predictors to one of the following layers as illustrated with dashed lines from  $x_5$  to  $z_6$  in Fig. 4. Consequently, the end-product of the output layer is the most suitable mathematical equation in proving the relation between predictors and target variable [18]. Furthermore, if n is the number of neurons in a layer, then the number of candidate neurons in the following layer can be computed as  $\frac{n(n-1)}{2}$  for two variable polynomials [19].

In this paper, the GMDH networks are chosen as a forecasting method due to its capability of creating mathematical model for analyses, its structural and parametrical configurability [16].

#### Support Vector Machines



Fig. 5. Nonlinear to linear mapping with SVM

SVM is a machine learning technique for binary classification problems. With an extension to SVM, the technique may also be implemented to regression problems (i.e. SVR that stands for support vector regression) for function estimation [20]. SVR is utilised to constitute a quite flat function f(x), which is a linear regression function, that has the capability to get the nearest vector representing the real output with a tolerance  $\varepsilon$  indicating error term. Energy forecasting has nonlinear solutions just as most problems encountered on the Earth, hence input data are mapped into a higher-dimensional space by using SVR in order to find out probable linearities for training data, and linear regression technique can be applied to the consequent space

$$f(x) = \omega \cdot \varphi(x) + b \tag{8}$$

where  $\varphi(x)$  is a function used for mapping from nonlinear space to linear space as shown in Fig. 5, and *b* corresponds to the bias [21]. In order to guarantee the flatness of f(x), a function having a minimum norm value of  $||\omega||^2$  should be obtained for each residual possessing a value smaller than  $\varepsilon$  [22]. In practice, a cost can be defined for residuals that are not smaller than or equal to  $\varepsilon$ , because such function may not be obtained. For this optimisation problem, the formulation of nonlinear  $\varepsilon$ -insensitive SVR ( $\varepsilon$ -SVR) is as follows

$$\min_{\omega,b} \frac{1}{2} \omega^2 + C \sum_{i=1}^{1} (\xi_i + \xi_i^*)$$
(9)

$$s.t.\begin{cases} y_i - f(x) \le \varepsilon + \xi_i \\ f(x) - y_i \le \varepsilon + \xi_i^* \\ \xi_i, \xi_i^* \ge 0 \end{cases}$$
(10)

where the penalty imposed on observations that lie outside the  $\varepsilon$  margin is controlled by C and shown by  $\xi_i$  and  $\xi_i^*$ . The dual optimisation problem of  $\varepsilon$ -SVR can be acquired by introducing a Lagrangian function with multipliers  $\alpha_j$  and  $\alpha_j^*$ . Each instance must conform to Karush-Kuhn-Tucker (KKT) conditions as well. Lagrangian multipliers for all instances throughout the margin are zero. Instances having multipliers that are not equal to zero are support vectors. In that case, the function f(x) is stated as

$$f(x_i) = \sum_{j=1}^{l} (a_j - a_j^*) K(x_i, x_j) + b$$
(11)

where  $K(x_i, x_j)$  is a nonlinear kernel function [23]. Linear, sigmoid, polynomial, and Gaussian RBF are universally utilised kernels. Due to its simpleness and computational efficiency over

the years, RBF kernel has been qualified as one of the best kernels [24]. RBF kernel function is expressed as

$$K(x_i, x_j) = \exp\left(-\frac{\left|\left|x_i - x_j\right|\right|^2}{2\sigma^2}\right)$$
(12)

where  $x_i$  and  $x_j$  are input instances,  $\sigma^2$  is variance, and  $||x_i - x_j||^2$  can be described as the squared Euclidean distance among two instances [23].

Moreover, cost (*C*) controls the SVR model's empirical risk degree, gamma ( $\gamma = \frac{1}{2\sigma^2}$ ) controls the Gaussian function width, and epsilon ( $\varepsilon$ ) controls the  $\varepsilon$ -insensitive zone's width sequentially. For the performance of SVR models, *C*,  $\gamma$ , and  $\varepsilon$  parameters should be well-determined in order to have a more accurate  $\varepsilon$ -SVR model [22, 25].

In this paper, the SVM are chosen as a forecasting method due to their ability to be performed with less parameters, their kernel trick which simplifies nonlinear relationships into linear ones by mapping, and their capability in improving generalisation performance [16].

#### **RESULTS AND DISCUSSION**

All computations in this paper were implemented on a Macintosh computer with an OS version of 11.2.2, a processor of 3.6 GHz (Intel Core i9), and a memory size of 8 GB by using RStudio with a version of 1.4.1103.

For GBDT, model parameters were canonically determined as 10 and 400 for the number of minimum and maximum trees in a series, 5 for the depth of individual trees, 10 for minimum size node for splitting, 50% for the proportion of rows per tree, 90% for Huber's loss function quantile cut-off, 1% for trimming factor influence, and 5 for the number of minimum spikes for smoothing according to the reputable studies in the literature. Moreover, pruning of series was carried out according to minimum absolute error, and equal predictor weights were applied.

For GMDH networks, the reference function with two variables was preferred due to its frequent use in the literature. Parameters were employed as 20 for the number of maximum network layers and 24 for neurons per layer as much as the number of predictors. Other parameters were confined such that 16 for the highest polynomial order and  $10^{-4}$  for convergence tolerance. Network configuration for the neurons in the next layer was adjusted as the selection of neurons in the previous layer and original predictors.

For SVM,  $\varepsilon$ -SVR regression was performed with a Gaussian RBF kernel. For hypertuning the model parameters, grid and pattern searches were used along with 4-fold cross validation in reference to minimising total error. Search ranges for model parameters were from 10<sup>-1</sup> to 5,000 for *C*, between 10<sup>-3</sup> and 50 for  $\gamma$ , and among 10<sup>-4</sup> and 100 for  $\varepsilon$  respectively.

In all models, the simple random sampling method was used to validate such that 80% and 20% of the whole data set were constructed for training and test sets sequentially.

According to the obtained results indicated in Table 1, the SVM model reached the lowest mean absolute percentage error (MAPE) and mean absolute error (MAE). Model utilising GMDH networks had the highest coefficient of determination ( $R^2$ ).

Forecasting	MAPE	MAE	$\mathbf{R}^2$
Method	(%)	(VAR)	(%)
SVM	3.22	6.55	98.47
GMDH Networks	3.37	8.62	99.08
GBDT	3.75	9.59	98.76

Table 1. Performance results of the applied forecasting methods

For discussion, performing models of GBDT and GMDH networks took up seconds while implementing the SVM model occupied days owing to the grid and pattern search with cross validation when the computational time was taken into account. To reduce the computational time in the SVM model, limit values of grid and pattern search should be determined very carefully. Using GBDT and GMDH networks for short-term reactive power forecasting is highly recommended because of its higher accuracy within very low computational time. It should be noted that if accuracy is the supreme concern, then SVM may be considered.

Furthermore, sensitivity analyses showed that the most efficacious predictors for shortterm reactive power forecasting are previous hour reactive power, real power, and complex power.

## CONCLUSIONS

Recently, energy forecasting applications have become important after the developments in smart grid technologies. As one of the energy forecasting applications, reactive power forecasting plays a crucial role in the energy management and planning of all facilities supplied by the distribution network.

Uninterrupted energy flow has utmost importance for hospitals owing to their continuous duty. Short-term reactive power forecasting is an essential tool in ensuring voltage stability, monitoring reactive power consumption, finding base and peak demands, minimising risks, and making viable decisions.

In this paper, real-time short-term reactive power forecasting using machine learning algorithms including GBDT, GMDH networks, and SVM were performed for a nonindustrial building complex. The results demonstrated that GBDT and GMDH networks have higher accuracies within a very low computational time range. Additionally, it should be noted that previous hour reactive power, real power, and complex power are predominant predictors in forecasting short-term reactive power.

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# ACCOMPLISHMENT OF VIBROACOUSTIC DIAGNOSTIC TASK OF TECHNICAL CONDITION OF MACHINERY AND EQUIPMENT USING THE MATHCAD SOFTWARE

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#### ABSTRACT

The article considers the importance of studying the vibroacoustic processes in the field of controlling and diagnosing the technical condition of machinery and equipment. As is well-known, failures in any mechanical system are reflected first in the vibration characteristics, and then, there are observed: noise, temperature rise, smell and smoke (just before the accident). It is in respect of these circumstances that noise and vibration are the main control parameters for detecting the newly-emerged defects. The basis of any modern system of vibroacoustic diagnostics of the technical condition of machinery and equipment is a digital analyser of the vibroacoustic signals, which is considered in the article, and its quality and accuracy are what determine the reliability of a diagnostic system. The expensiveness of the existing digital analysers and diagnostics programs on the world market forces us to create and develop the alternative programs. To that end, a digital analyser was developed in a computer mathematics system MathCad, which can be used for vibroacoustic diagnostics and monitoring. The use of MathCad as a software environment has resulted in a high accuracy and universality of this digital analyser.

The article presents as an example the stages and steps of accomplishing vibroacoustic diagnostics of the technical condition of machinery and equipment created using the MathCad software. The basis for accomplishing this task is a digital analyser of the vibroacoustic signals in a MathCad package. The article provides the examples of input of the real vibration signals in this analyser, FFT (Fast Fourier Transformation) spectral representation of signal, cepstrum, filtration, and so on. Also, the article provides the examples of vibration signal modelling, diagnosis, and using the logic block "if - then".

**Keywords:** Digital analyser, Vibroacoustic diagnostics, MathCAD software.

#### 1. INTRODUCTION

In world practice, the problem of ensuring the reliability of technical systems in their operation remains topical [6]. This is attested to by more frequent breakdowns and failures at various sites, for example, the tragedy at the Sayano-Shushenskaya HPP (August 17, 2009) and environmental disaster in the Gulf of Mexico (April 20, 2010).

The only proper way to protect mechanical devices from major disasters, as well as to avoid minor accidents and malfunctions, is to ensure continuous monitoring, analysis and diagnosis of technical systems in the course of their operation [6]. At the same time, it is necessary to take all necessary regulatory measures at the appropriate time. Further improvements in reliability, quality and performance of mechanical systems can only be achieved through introduction of highly-efficient methods and tools of technical diagnostics [9].

When developing modern methods for control and diagnosis of technical condition of machinery, particular importance is given to the analysis of vibroacoustic processes. In world practice, the systems of technical condition monitoring and vibration control are increasingly being introduced, and they significantly increase the duration and effectiveness of operation of

the equipment without any major repairs and reduce maintenance and repair costs. The risk of failures and breakdowns is also reduced [7].

It is known that at the time of any changes (including degradation changes) in the mechanical systems, shortcomings in technical condition of the system are more evident in the vibration characteristics, and then in a chronological order, there occur: noise, temperature rise, smell and smoke (just before the breakdown). It is in respect of these circumstances that noise and vibration are the main control parameters for detecting newly-emerged defects [6].

The basis of any modern system of vibroacoustic diagnostics of technical condition of machinery and equipment is a digital vibroacoustic signal analyser, whose quality and accuracy determine the reliability of diagnosis [7].

#### 2. RESEARCH SUBJECTS

The high cost of the digital analysers and diagnosis programs available on the world market forces us to design and develop alternative programs. To this end, a digital analyser was developed in a math software Mathcad for vibroacoustic diagnostics of technical condition of machinery and equipment to diagnose the machine's technical conditions. The use of Mathcad as a software environment has secured high accuracy and the universality of a digital analyser.

It is well known that Mathcad differs from other math software in the simplicity of the "language of communication" and has a unique ability to describe the mathematical algorithms using the generally accepted characters in the natural mathematical form, which greatly facilitates perception of mathematical sense of tasks to be accomplished [10].

The mathematical environment of a digital analyser greatly expands its capabilities, allows us for making high precise calculations, and imparts the analyser practical universality. The analyser is indispensable for solving research and educational tasks, modelling vibroacoustic signals, as well as in the process of designing and developing the expert and automated diagnostic systems.

When diagnosing machine (or its individual part), the digital analyser processes the vibroacoustic signals removed by means of the sensors, extracts useful information from it, analyses and compares the signal parameters with the values of previous measurement and allowable parameters, while the probable symptoms of equipment troubles and the allowed values for the parameters are known in advance and included in the algorithms of diagnosis.

#### 3. PREPARING INITIAL DATA

The signal that goes into a digital analyser must be recorded in \* .wav format of a sound file and placed in the Digital Analyzer folder. Then, opening this folder and the Mathcad files contained therein directly produce results of complete signal processing, which is essential for diagnostics of technical condition of machine [5].

To enter the actual signal into the computer, there can also be used the computer's microphone input and small computer program Spectra-Lab (Sound Technology Inc.). The signal will be recorded in \* .wav format, which can then be processed in a digital analyser or in the Spectra-Lab program.

It is known that the maximum frequency of the sound heard by a human is 20 kHz. During the digital processing of signals, the computer's analog-to-digital converter cuts out some of the time segments from the analog signal, provides its discretization and digital recording. According to the Nyquist theorem, the number of discrete readings of the cut-out time realizations should be double the value of the maximum frequency of harmonics existing in the spectrum. So, when recording the signal in the computer, we take 44.1 kHz as the discretization

frequency, which corresponds to a maximum direct frequency limit of 22.05 kHz. In the case of other frequency bands, we need to take the appropriate analog-to-digital converter [4].

Each time realization is quantized by 16 bits and the levels of different readings are 216 = 65 536 different values. To read out signal information from a \* .wav file, Mathcad uses the function GETWAVINFO, which rotates 4-dimensional vector Figure 1.



Fig. 1. An example of presenting information on the signal in MathCad

Here, NumChanels = 1 is a channel count value, SampleRate = 44100 – sampling rate, Resolution = 16, number of bits (i.e., 2 bytes), AavgBytesPerSecond = 88200 - Average conversion speed (BPS).

Figure 2 below illustrates an example of the input and visualization in Mathcad of the radial vibration signal removed from the transmitters mounted on the turbines.



Fig. 2. An example of the input in and visualization real signal in Mathcad

The mathematical environment of the analyser allows us for computing easily the values required for diagnostics, for example, the root mean square value of signal (RMS), which is proportional to the vibrating power, as well as the CrestFactor-i, which is the ratio of the signal maximum to the RMS, and so on.

Note that RMS and CrestFactor are the important parameters to assess changes in the process of vibroacoustic diagnostics of technical condition [3].

FFT (Fast Fourier Transformation) spectral representation of signal in a Mathcad environment is performed by means of special operators. Fig. 3 illustrates the result of the narrowband spectral analysis of the above-mentioned signal.



Fig. 3. Signal spectral representation

At the top of the diagram, there are plotted the harmonics numbers (the rotational frequency is f1 = 61.235 Hz). In the range of 1000 Hz, there are clearly visible16harmonics, of which the fourth is the maximum.

Detection of the periodicity concealed in the signal in vibrodiagnostics of machinery is carried out using the cepstrum which represents the inverse Fourier transformation performed on the signal logarithm [1]

$$k_{x}(n) = 1/2\pi \left[\int_{-\pi}^{\pi} \left(\ln((|X(\omega)|)e^{j\omega n})d\omega\right].$$
(1)

In practice, the cepstrum is often defined as the conversion of a narrowband spectrum. Figure4 shows the cepstrum of the above-mentioned signal, which clearly illustrates the harmonic constituents with a fundamental frequency of 61,235 Hz.



Fig. 4. Vibro-signal's cepstrum in Mathcad

Impulse, nonlinear, random vibrations and auto-oscillations generate the modulated signals in the machine, the analysis of which require the high-frequency filtering of the outgoing signal Fig. 5, finding its envelope and the low-frequency analysis of this envelope Fig. 6 [4].



Fig. 5. The high-frequency filtering of the outgoing vibro-signal



Fig. 6. The low-frequency spectrum of the vibration envelope in Mathcad

Fig. 5 illustrates a high-frequency filter of the outgoing vibrosignal, finding its envelope using the Hilbert transform, and then Fig. 6 shows the low-frequency spectrum of envelope, which is extremely important for vibroacoustic diagnostics of technical condition of machinery.

Consider the example of vibrating signal modelling in Mathcad. As is well known, if in the spectrum of vibrating signals, the constituents are visible on the so-called "side" frequencies, this may be due to modulated oscillations generated in the machine [8]. The upper part of Fig. 7 illustrates an analytical image of modulated oscillation, where f2 is the carrier frequency, f1 – the modulation frequency, n – the depth of modulation. In the upper part of Figure 8, we can see 3 constituents of the spectrum, on the side frequencies (f1-f2) and (f1+f2) and the carrier frequency – f2. The drawing below illustrates the balanced of the signal envelope, where we can see only 1 constituent of modulation at f1 frequency. The diagrams clearly show how modulated oscillations affect the characteristics of the system, and where and how to search for the modulated elements in the complex real systems.



Fig.8. The same signal's spectrum (a); the spectrum of envelopes (b)

The analyser allows to use a powerful modern signal processing device (Signal Processing package) when required, and not only that. The Mathcad system's mathematical environment and state-of-the-art programming tools can be successfully used to build the comprehensive expert diagnostics systems.

In the event of the machine defects, for diagnosis, the logic block "if - then" is used in Mathcad block that compares output and permissible values and makes a diagnosis Figure 9.

 $\Delta 141 := 0.05$ D14 := "There is a defect"" if  $\Delta 141 \ge 0.2$ "There is no defect" otherwise
D14 = "There is no defect"

Fig. 9. The block for making a diagnosis in Mathcad

Mathcad is also convenient to use in the process of designing and creating the automated diagnostics systems, since it easily removes harmonics, sums, maximums, and other integral characteristics from the signal. Mathcad also allows to build the self-learning expert systems and the artificially intelligent systems. Mathcad is compatible with applications such as Matlab, LabView as well as Excel, Word, etc.

## CONCLUSION

Mathcad software can be successfully used as a digital analyser in vibroacoustic diagnostics of the technical condition of vehicle.

The digital analyser considered in this article can be used as an automated tool for the creation and development of vibroacoustic diagnostic systems.

The introduction of a digital analyser in practice will allow us to monitor the technical condition of the car during the operation process.

This digital diagnostic analyser can be used in any area of engineering after making appropriate modifications.

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# **CONFERENCE PAPERS**

# **II. PHYSICAL SCIENCES**

# II.1. Combustion and plasma processes

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# NUMERICAL MODELLING OF TURBULENT COMBUSTION IN A SMALL-SCALE VENTING CHAMBER

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#### **EXTENDED ABSTRACT**

Increasing role of hydrogen in renewable energy applications necessitates additional attention to the safety issues, since hydrogen can form explosive mixtures with air, which can produce higher explosion overpressures and flame speeds and can cause more damage than methane or propane explosions. Most of the current research oriented turbulent hydrogen combustion simulations are based on LES and combustion models based on chemical reaction rates. However, practical applications, especially of larger scale, are still mainly accessible only with RANS simulations. Combustion models can be further simplified substituting reaction rate models with semi-empirical correlations, which relate turbulent conditions and flame propagation speed. One of the most common such approaches is turbulent flame speed closure (TFC) model.

While RANS/TFC are simplified models advantages of which are mostly evident in larger scale simulations, it is also important to validate them at laboratory scale as well, which is convenient for more detailed analysis of model capabilities. Small-scale venting combustion chamber located at the University of Sydney was used to investigate interaction of turbulent premixed flame with several obstacles. Obstructions in the direction of flow caused a complex flame front interaction with the turbulence generated ahead of it. The flame front-turbulence interaction is responsible for the combustion rate, the rate of pressure rise and achieved overpressure, the geometry of accelerating flame front and resulting structures in the flow field.

This paper reports RANS/TFC simulation of turbulent hydrogen combustion and flame propagation in the University of Sydney small-scale combustion chamber using OpenFOAM CFD toolkit and custom-built turbulent combustion solver based on the progress variable model – flameFoam. Numerical validation results showed a well reproduced pressure behaviour. The analysis revealed that as the propagating flame reaches and interacts with obstacles, the recirculation wakes of flow is created behind solid obstacles leaving traces of unburned mixture. The expansion of flames due to narrow vents generates turbulent eddies, which cause increase of flame area and wrinkling of the flame front.

Simulations performed using flameFoam solver withs RANS and TFC models were able to adequately reproduce observed pressure behaviour in the simulated case. The maximum overpressure value of 0.8 bar and its timing were correctly predicted in the simulation. A brief period of pressure stagnation was not predicted, possibly due to missing quenching process model in flameFoam. Flame propagation and flow configuration study showed that vortices were formed behind the obstructions in front of the flame. Vorticity increased with the height of the obstacles, due to larger flame and flow velocities. A positive feedback loop was thus formed – with increasing propagation velocity interaction with obstacles lead to more intense turbulence and higher vorticities, while stronger vortices lead to increased perturbation and stretching of flame front, which in turn lead to faster combustion and even higher propagation velocities. The flame interaction with vortices resulted not only in wrinkled flame front but

also in the flame being pulled into vortices, consequently intensifying the mixing of unburned (vortex core) and burned mixtures.

**Keywords:** flow structures, turbulent flame propagation, hydrogen combustion, computational fluid dynamics (CFD), industrial safety

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# NUMERICAL MODELLING OF TURBULENT HYDROGEN-AIR-DILUENTS MIXTURE COMBUSTION IN THE ENACCEF FACILITY

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#### **EXTENDED ABSTRACT**

Severe accident in the nuclear power plants can pose a severe threat in terms of hydrogen production and combustion. In case of containment integrity failure as a result of hydrogen gas deflagration and detonation, the fission products might be released to the atmosphere. In a severe accident scenario, hydrogen generation, deflagration and detonation phenomena are very important. Therefore, benchmarks, experiments in different facilities, development of custom codes, usage of regular packages in order to model processes are being done in order to understand and be able to foresee and mitigate possible risks.

This paper deals with hydrogen flame propagation experiments performed in ENACCEF facility. This facility consists of two sections – a vertical acceleration tube with 9 obstacles and a dome used for the experiments of flame acceleration. Therefore, some benchmarks use its data to test and adjust existing CFD models and to validate created custom solvers.

SARNET H2 benchmark focused on turbulence effect on flame propagation. Obstacle induced turbulence is concern to nuclear safety due to faster combustion process which can result in a more severe explosion as a consequence of a faster rate of pressure rise. Furthermore, turbulent combustion is even more complex because of coupling between chemistry, mass/heat transport and fluid dynamics. There is still a lack of understanding for the turbulent flame propagation mechanisms for this phenomenon. Nevertheless, efforts are being made in interpretation of combustion and turbulent flame speed concerning correlations and models. In premixed turbulent combustion turbulent burning velocity is more important than mixing, because reaction speed depend on the first. Thus, selection of suitable turbulence model is very important, whereas erroneously calculated turbulence can be the issue of uneven and huge increase of velocity and pressure.

Two-dimensional computational fluid dynamics simulation of SARNET H2 benchmark of turbulent flame propagation in the ENACCEF facility was carried out. Modelling was done with mixture of 13 % H<sub>2</sub> with air and considering different diluents concentrations – 0 %/ 10 %/ 20%/ 30%. Simulations not only provides information about hydrogen combustion but also validates the custom-build turbulent combustion solver – flameFoam, which is based on the progress variable approach. Moreover, solver implements several turbulent flame speed correlations, based on which parametric analysis was performed together with turbulence model to better understand k- $\omega$  SST model blending function behaviour.

Results show that Zimont turbulent flame speed correlation allowed to obtain results closest to experimental data, while Bray and Bradley overestimated flame velocity. Additionally, k- $\varepsilon$  turbulence model was more suitable for turbulence modelling, whereas k- $\omega$  SST model generated more turbulence in the steep velocity gradient zones near obstacles resulting in erroneous results. Also, less diluents in the mixture give rise to a higher pressure load and a faster turbulent combustion.

**Keywords:** Premixed turbulent combustion, flame propagation, combustion solver, computational fluid dynamics (CFD), hydrogen safety

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# REVIEW ON SOLID WASTE UTILIZATION IN THERMAL PLASMA ENVIRONMENT

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#### ABSTRACT

Since the beginning of industrialization, various materials for human needs have been used and recycled globally. Some of the wastes can be used as secondary raw materials in production processes. However, a significant part of it is released into the environment as pollutants. Therefore, waste management is becoming a major topic of public debate and research. Currently, waste management is based on the waste hierarchy principle, which became an integral part of the national and international regulations (e.g. the EU Waste Framework Directive 2008/98/EC). According to the waste management hierarchy, waste prevention, re-use, recycling, and recovery has become significant in recent years due to the limited availability of material resources in nature and the growing population in the world (the EU and especially in countries such as the US, China, India, etc.). Furthermore, the demand for energy produced is increasing rapidly due to technological development and increasing comfort of humans' lives. For this reason, efforts are made to find ways to convert certain types of waste into various types of fuel (biodiesel, synthetic gas, hydrogen, etc.). As a result, many waste disposal methods (incineration, pyrolysis, plasma-chemical decomposition, etc.) have been developed or is in a developing stage.

Nowadays, plasma gasification is mostly limited to lab or pilot scales. It is because of various challenges associated with it. The most important is the existing knowledge gaps which need attention and research for its successful future commercialization. The process of conversion of waste using ionized gas plasma has been extensively studied. Plasma is an aggregate state of matter consisting of free electrons, ions, and neutral particles. The decontamination of various organic wastes by conventional thermal methods (low-temperature oxidation, distillation, desorption) usually results in temperatures below 1300–1500 °C. However, not all materials are properly digested by these methods. Some toxic organic secondary compounds such as dioxins, furans, and others containing chlorine cannot be degraded under these conditions. In order to completely decompose such materials, the reaction temperature must be raised to 1800 °C and maintained in the reaction zone for 1–2 seconds. Such conditions can only be achieved in a plasma-chemical reactor fed with a flow of various gases (air, water vapor, hydrogen, etc.) heated by a plasma torch up to 3000 °C and above. In this process, the molecules of the processed waste are broken down into atoms, radicals, electrons and positive ions. This paper reviews the potential of thermal plasma application for solid waste treatment with a special focus on municipal solid waste treatment.

Keywords: thermal plasma, arc discharge, solid waste, syngas.

#### **INTRODUCTION**

Municipal solid waste (MSW) is generated in large quantities worldwide. It is expected the increase of MSW due to swift urbanization and the change in lifestyle. Approximately 1.5 billion metric tons per year of MSW was produced in recent years [1]. Household waste accounts for less than a tenth of the 2.5 billion tons of total waste generated in the European Union each year. Average household waste per capita in the EU in the period 2005–2016 decreased by 7%. However, trends vary from country to country. For example, waste increased in Denmark, Luxembourg, Slovakia, Croatia, Germany, Greece, Malta, the Czech Republic, Latvia as well as Lithuania, while it decreased in Bulgaria, Spain, Hungary, Romania, the Netherlands, Ireland, Estonia, Belgium, Italy, Sweden, Cyprus. Denmark has the highest levels of household waste in 2019. In general, more waste per capita is generated in richer and more developed countries with higher consumption level. On average, about 472 kg of

household waste per capita was generated in Lithuania in 2019, while in 2005, it was only 387 kg. These data are represented graphically in Figure 1.



# Municipal waste generated, 2005 and 2019

Note: Countries are ranked in increasing order by municipal waste generation in 201 (\*) Estimated. (2) Bulgaria, Ireland, United Kingdom 2018 data, Iceland 2017 data

Source: Eurostat (online data code: env\_wasmun)

eurostat O

#### Fig. 1. Municipal waste generated in 2005 and 2019 in EU member states, Iceland, Switzerland, Norway and United Kingdom [2]

Members of the European Parliament (MEPs) welcomed the update of EU waste management rules, including new binding targets for municipal waste recycling and landfill, as well as packaging recycling in Strasbourg, 2018 April 18. Rapid accumulation of MSW, increasing cost of landfills, and landfill problems (e.g. toxins and leachate) obligate governments to seek solutions and find new sustainable techniques to dispose of MSW cost-effectively. The aim of the new rules is to encourage the transition to efficient and sustainable use of resources, the so-called circular economy. For the circular economy, waste needs to be transformed into value (waste-to-resource (e.g. energy)) through effective waste treatment.

According to Eurostat data, about 48% of all household waste was recycled or composted in 2019. However, when waste recycling and recovery options are limited, energy recovery can be applied as the best option avoiding its disposal on landfills. Usually, waste and its harmfulness are characterized by its origin, classification, physical and chemical properties and other parameters (Fig. 2) [2].



Fig. 2. Waste classification, adapted from [3]

The quantities and vast diversity of waste make it quite difficult to establish a waste classification (waste sorting). The solution to the problem of how to manage and utilize waste sources includes not only real-time waste generation but also the utilization of existing landfills. To summarize the technological possibilities of waste recovery, three main directions of waste circulation can be defined, which are presented in Fig. 3 [4–6].



Fig. 3. Waste use alternatives, adapted from [6]

There are plenty of techniques for MSW disposal and processing. Such waste may be treated using biological, hydrothermal, and thermochemical (e.g. gasification, pyrolysis, and incineration) techniques [6-9]. Each of these technologies has its advantages and limitations (types of materials to be degraded, their concentrations, etc.). The biological techniques are environmentally 'safe' but time-consuming and sensitive to environmental change (e.g. temperature shocks). To convert MSW to biogas or compost requires a large area and time. Thus, the biological degradation of MSW is a slow process. Furthermore, these techniques are unsuitable for converting the waste containing less organic matter and inefficient for hazardous waste.
Hydrothermal techniques are relatively faster and environmentally 'safe' too. The application of these technologies allows to reduce the volume of MSW and at the same time extract valuables from waste. However, these technologies have higher operational costs due to associated energy costs. Also, hydrothermal technologies are not operationally 'safe' as they have associated safety issues due to the required extreme conditions (high temperature, pressure).

MSW could be converted to charcoal, oil, syngas, or heat using thermochemical techniques, which, to some extent, are environmentally 'safe' too, but have high operational costs.

Of the many methods currently used to decontaminate MSW materials, thermal methods are the most widely used. The most universal of these is the flame method (waste incineration) [3], but not sufficient as it is not possible to neutralize waste which decomposes at temperatures of 1800 °C and higher. According to the literature, incineration [14–16], gasification [11,18– 20], and pyrolysis [21–24] are thermochemical techniques mostly utilized for waste disposal. So far, plasma gasification has mainly been used for treating hazardous waste, and its use for waste-to-energy processing is a relatively new topic. Despite that, the technology requires high capital and operational costs and is a highly energy-intensive process, but the treatment efficiency is very high, up to 99.99%. The limited plasma technology commercialization success and currently limited process understanding results in a rather narrow application at an industrial scale. Nevertheless, the potential and interest in applying or combining plasma technologies with traditional methods attract attention. The flame method is often combined with plasma waste neutralization to reach higher treatment efficiency and reduce costs. In order to completely decompose toxic substances, the reaction temperature must be raised up to 1800 °C and maintained in the reaction zone for 1–2 s [5,6]. Such conditions are only achieved using plasma technology [7,8].

The purpose of this paper is to review the applicability of the plasma-chemical waste neutralization method and analyse the potential of plasma for solid municipal waste treatment. Based on the gathered information, the paper is written to lead firstly to the explanation of the plasma classification and plasma gasification process (section 2). Then, in section 3, the main working principle of the plasma generators, which works at atmospheric pressure, are presented. Also, various factors on which the solid waste neutralization process depend is provided in this section. Section 4 shortly introduces the thermal methods for the decomposition of the waste. Then, the generalization of the thermal plasma treatment methods is presented in section 5. Finally, conclusions are given in section 6. The topic covered in this paper will assist those who deepen the understanding of the thermal plasma application for the solid waste conversion process.

### CLASSIFICATION OF PLASMA AND PLASMA GASIFICATION

Depending on the type and amount of power transferred to the plasma, the plasma electron density or temperature changes. These two parameters determine the plasma properties and differentiate into different categories (Fig. 4).



Fig. 4. Classification and categories of plasma [58]

Plasma is divided into relatively high (T> $10^5$  K) and low temperature (T< $10^5$  K). Hightemperature plasma is obtained during nuclear fission and fusion reactions. Low-temperature plasma is obtained by arc discharge and is widely used in various material manufacturing processes. Solid-state processing technologies use glowing discharge plasma at temperatures close to ambient. Gas can be converted into plasma not only by heating but also by the use of short-wave high-frequency electromagnetic radiation [5,10–13]. Plasma is the fourth state of matter, obtained by breaking atoms and molecules down to constituent ions and electrons after electrifying a gas [30].

Plasma gasification is a thermal process in which waste is exposed to extreme thermal conditions (approximately 2000–14000 °C). Fig. 5 shows a schematic of plasma gasification of MSW. Multiple stages are involved in the plasma gasification of MSW (waste handling, the plasma gasifier, gas cleaning, and conversion unit processes). MSW is exposed to plasma heat in the presence of an oxidant which converts the waste into syngas and inert slag [27], Fig. 5. Various gases such as nitrogen, argon, hydrogen, carbon monoxide and carbon dioxide may be used for creating plasma. A plasma gasifier produces raw syngas, which contains particulates, and requires cooling, cleaning, and further conversion into synthetic fuels, hydrogen, and alcohols. It is important to mention that plasma gasification reactions are divided into oxidation reactions with oxygen, gasification reactions with steam, hydrogen, and carbon dioxide, and the decomposition of tars and hydrocarbons [17].



Fig. 5. Plasma gasification schematic [54]

Plasma gasification reactions take place when the ratio of oxygen to carbon molecules is less than one. During the plasma gasification process, nitrogen and sulphur in the feedstock convert to nitrogen and hydrogen sulphide, avoiding nitrogen oxide (NOx) and sulphur dioxide (SO<sub>2</sub>) formation. Furthermore, inorganic acid halides are formed from halogens in the feedstock.

In some recent studies, plasma gasification has been demonstrated as an effective and environmentally friendly technology for waste disposal. Plasma gasification is used to recover energy from plastic solids [31–36], MSW [8,30,36–38] biomass [40–44], used tires [45,46]. Also, to treat hazardous biomedical waste [46–49] or waste from the oil and gas industry [50–52], and applied in metal recovery from metal-containing waste [28,52,53]. So, it is evident that plasma gasification of waste (e.g. MSW) can reduce the need for landfills, produce syngas or energy from waste, and dispose of hazardous waste without leaving ash [29].

The plasma gasification process has various design characteristics. The main characteristics are the gasifier configuration, the feeding mechanism, the accumulation and collection of syngas and slag. Plasma gasifiers are classified into three main types: plasma entrained bed gasifiers (feed or MSW is injected with plasma gas as input stream(s), and syngas and slag are collected from the output stream(s) of the gasifier), plasma fixed-bed gasifiers (feed is in the form of fixed bed or batch mode; plasma is injected into the fixed bed, syngas can be collected from the upper part of the gasifier; slag is collected at the bottom), and plasma moving-bed gasifiers (feed is fed continuously into the top and out from the bottom of the gasifier; plasma is injected into the feed flow) [25,37].

The main operating parameters that affect plasma gasification are 1) the gasifier reaction temperature (2000–14000 °C), 2) residence time (30 min to 180 min), 3) the flowrates of the plasma gas, oxidant, and steam streams [33].

### ATMOSPHERIC PRESSURE PLASMA AND ITS SOURCES

Plasma generators, also known as plasmatrons, are commonly used to obtain atmospheric pressure plasma. The operation of plasma generators is based on the physical principles of electric arc discharge. Electric arc discharge plasma at a pressure close to atmospheric pressure can be formed between two electrodes (cathode and anode) due to caused high-frequency short duration discharge. When the plasma generator emits electrons from the cathode, an electric current of sufficient density is generated to provide the energy transfer within the arc itself. At a high-voltage pulse between the cathode and the anode, high-energy electrons are emitted by thermoelectronic emission, which ionizes the gas in the pre-anodic region. In this way, the electric arc discharge is obtained in the presence of impact ionization due to accelerated electrons. The electric arc discharge involves complex gas dynamics, heat and mass exchange processes, and other physical phenomena. Electric arc discharge is supported by the direct current (DC) power supply. The temperature of ionizing particles forming atmospheric pressure plasma depends on the current strength. The plasma temperature of the electric arc discharge can reach 2500-20000 K (or 0.25-2 eV). The gases most commonly used to form the atmospheric pressure plasma jet are argon, nitrogen, helium, hydrogen, water vapor, air, and mixtures of these gases. The electric arc discharge is divided into high (P> $10^3$  Pa) and low pressure ( $P < 10^3$  Pa). For low-pressure plasma, the temperature of electrons is tens of thousands of Kelvin higher than that of ions and neutral particles. This is because, in the case of lowpressure plasma, the free path of electrons is larger than in the case of high-pressure plasma. As a result, they are more accelerated by the electric field, which results in higher electron temperatures [24].

The technological purpose (waste utilization, organic fuel conversion, coating formation, etc.) of the plasma generator is strongly influenced by its operating parameters: power,

efficiency, plasma flow enthalpy, its temperature and speed. They can be calculated according to the given methodology [14–16].

The plasma-chemical reactor (schematically shown in Fig. 6), which is fed with specially prepared waste (granular or crushed down to millimeter size), is a chamber consisting of individual cooled sections connected to a plasma generator.



Fig. 6. Schematic view of a plasma-chemical reactor, adapted from [60]

A high temperature (3000–4000 °C and above) is reached in the plasma arc reaction zone of the plasma generator, where chemical reactions leading to the decomposition of contaminants take place. In addition, the plasma is a unique environment in which all chemical reactions that are not possible in the usual environment of combustion products can take place [39].

The process of neutralization of solid waste depends on many factors: properties of plasma forming gas, distribution of plasma flow temperature, flow rate, cooling water temperature, design parameters of the plasma-chemical reactor (exit diameter, reactor channel length, etc.), ionization level of plasma, the residence time of degraded material in the reaction zone, etc. [16–18]. Therefore, during the operation, the basic parameters of the experimental equipment must be measured and strictly controlled [24–26].

# THERMAL METHODS FOR WASTE DECOMPOSITION

Environmentally hazardous waste using thermal methods is decomposed in a hightemperature environment. The possibilities of thermal waste decomposition methods are given in Table 1.

Pyrolysis involves the decomposition of dangerous substances without oxygen. The pyrolysis method is carried out at temperatures of 400–650°C depending on the type and composition of the degradable materials. Pyrolysis yields a variety of liquid, solid and gaseous products: CO, CO<sub>2</sub>, H<sub>2</sub>, CH<sub>4</sub>, water, carbon, slag [19,20].

Waste neutralization method	The phase of neutralized waste	Advantages of the method	Weaknesses of the method
Heterogeneous catalysis method	Gaseous waste	Easy realization	Low temperature (up to 850 °C). Additional catalysts are required. Not

Table 1. Comparison of thermal waste decomposition methods [59]

			suitable for liquid and solid waste.
Pyrolysis	Gaseous, liquid and solid wastes	No air needed	Limited process temperature (up to 1050 °C)
Waste gasification	Liquid and solid wastes	Adjustable calorific value of incoming gas	Not suitable for neutralization of gaseous waste
Flame method	Gaseous, liquid and solid wastes	Versatility. During neutralization, there are almost no by-products.	Limited temperature (1300 °C)
Plasma-chemical method	Gaseous, liquid and solid wastes	High process temperature (up to 20000 °C and above), high efficiency (up to 99 %), versatility.	High-energy consumption. Fast wear of plasma generator parts. The cost of the device.

Waste gasification occurs when air, water vapor or mixtures thereof are blown into the combustible material. In this way, the waste is partially incinerated and gasified. The type of gas injected and the combustion conditions determine the calorific value of the obtained secondary gas. Waste gasification differs from flame combustion because it produces flammable gas (generator gas), which can be used as an energy fuel in the production of heat, electricity, chemicals or biofuels.

Meanwhile, the flame method is one of the most versatile methods used in waste decomposition processes. This method incinerates the waste at temperatures from 1200 to 1300  $^{\circ}$ C by injecting air or an oxygen/air mixture.

However, the main disadvantage of all these thermal methods is the relatively low process temperature (up to 1500 °C). In the environments with too low temperatures, while neutralizing waste, the secondary highly toxic substances such as dioxins, furans and others are produced, which are far more toxic than the primary products. In order to completely decompose the toxic substances, the ambient temperature should be raised to at least 1800 °C, and the waste should be kept in the reaction zone for 2–3 seconds. A plasma method is used to achieve these conditions, which allows the temperature to be reached between 3000 and 4000 °C and higher, if necessary. This method is implemented in plasma-chemical reactors using plasma of various gases (air, nitrogen, hydrogen, etc.). Currently, the plasma method is used for the decomposition of liquid and gaseous waste, where there are no possibilities to decompose it by the flame method. This method completely decomposes both the primary and secondary toxic substances. The efficiency of this method is up to 99.99 % [8].

Plasma gasification has a higher net annual revenue potential, a higher net energy production potential, and lower environmental impacts in comparison with other thermochemical technologies, such as incineration, pyrolysis, and gasification [55]. Plasma gasification shows better results in net energy production potential (816 kWh/ton of MSW) in comparison with pyrolysis (571 kWh/ton of MSW), incineration (544 kWh/ton of MSW) or gasification (685 kWh/ton of MSW) [54].

### **GENERALIZATION OF THERMAL PLASMA TREATMENT METHODS**

Plenty of authors in their papers argue that plasma gasification offers promising opportunities to convert MSW to value-added products. Also, there are problems with MSW

plasma gasification that need to be solved for successful industrial application. The main challenges associated with plasma gasification of waste by value are shown in Fig. 7.



Fig. 7. Challenges associated with plasma gasification for waste-to-value processing [5]

Plasma gasification is a relatively expensive technology for waste-to-value processing compared to other technologies, such as mentioned in the previous section pyrolysis and gasification. The economy of plasma gasification depends on many factors such as regional characteristics, plant capacity, the composition of MSW to be processed, and process parameters. No less important is the region characteristics such as local conventional technology costs, government regulations, support, etc. [56,57]. Plasma gasification requires sorting the incoming MSW because poorly sorted waste can adversely affect synthesis gas production and damage plasma gasifier refractory linings. Wet waste can adversely affect the yield of synthesis gas and requires more energy to process, as compared to dry waste.

Plasma gasification is considered a highly energy-intensive process. The waste decomposition processes create extreme temperature conditions using plasma to convert MSW to relatively clean synthesis gas and vitrified slag from the residual ash. A high amount of plasma energy is required to heat, melt, and finally vaporize waste for molecular dissociation and breaking apart molecular bonds to separate complex molecules into individual atoms in the gaseous phase [33]. A highly energy-intensive plasma gasification process requires massive amounts of expensive DC power supply. They can put an additional capacity load on the power grid and increase the operating cost of the process.

#### CONCLUSIONS

The thermal plasma technology is a promising solution for the various solid waste treatment and gasification such as automobile tires, plastics, petroleum process by-products, municipal waste, toxic or hazardous medical and electronic wastes. Plasma gasification could be proposed as a viable alternative solution for waste treatment with energy recovery. During this process, extremely high temperatures are reached, and the molecules of the waste to be processed are broken down into atoms, radicals, electrons and positive ions. As a result, very high efficiency of solid waste gasification is reached, and only non-toxic materials or products such as carbon, water vapor, etc., are formed. It was demonstrated that plasma gasification could be a suitable technology for waste-to-value processing for the circular economy. Despite this, there are various challenges associated with plasma gasification for MSW processing. It includes the reduction of the capital and operation cost, assurance of the proper waste sorting,

optimization and reduction of the process temperatures and increase of use of thermal plasma in combination with other waste treatment processes.

However, in order to successfully implement the plasma technologies for waste treatment on the industrial scale, several challenges should be solved.

The high energy plasma gasification process, while contributing to the greenhouse effect and costly is effective in decomposing waste that cannot be recycled.

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# PECULIARITIES OF PLASMA SPECTROSCOPY OF UNDERWATER ELECTRIC SPARK DISCHARGE BETWEEN MOLYBDENUM GRANULES

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#### ABSTRACT

This work is devoted to plasma emission spectroscopy of electric spark discharge, which is used for the synthesis of metal nanoparticles. The main aim is to investigate the possibilities of using of methods of such spectroscopy for determination of the key plasma parameters of such discharge, namely, excitation temperature and electron density, and, as a consequence, improve the process of metal nanoparticle synthesis.

The special attention is paid to peculiarities treatment of emission spectrum radiated by plasma of discharge between molybdenum granules immersed into water. Additionally, the behaviour of Balmer series spectral line of hydrogen, namely  $H_{\alpha}$ , in plasma emission of such discharges was investigated.

The specially developed pulse power source is used to initiate a discharge between copper granules immersed into the deionized water. Typical values of voltage vary from 40 to 200 V, current is up to 150 A and pulse frequency is in the range of 0.2-2 kHz. The voltage, applied to electrodes, caused a current flow along the chain of closely arranged granules in the stochastic switching mode.

Optical emission spectroscopy methods are used for diagnostics of such discharge plasma. The Boltzmann plots of metal atom lines' intensities are used to determine the plasma temperature. Preliminarily the spectral lines of metal atoms and spectroscopy data of these elements were carefully examined.

In the result of investigation the excitation temperature of underwater discharge between molybdenum granules was determine on the base of the previously selected and additionally proposed Mo I spectral lines, which led to an increase in accuracy of the temperature determination.

Profile of  $H_{\alpha}$  spectral line, exposed to the Stark mechanism of spectral lines' broadening, is used to determine the electron density.

It was concluded that it is important to take into account the all significant radiation from the considered spectral range, in particular, all spectral lines which can emitted, in order to correctly determine both the emission intensity of particular spectral line and its width

Keywords: emission, plasma parameters, underwater discharge, metal granules, Stark effect

#### **INTRODUCTION**

Currently, the electric discharges burning in the liquid, in particular, water, are of great interest. Among the numerous applications of such discharges, the synthesis of nanoparticles is most relevant and demanded issue among scientists. This is caused by widespread use of nanoparticles in various branches. For example, magnetic iron oxide nanoparticles are becoming widely used in biomedical applications for developing magnetic resonance imaging contrast agents as well as biocompatible and biodegradable drug carriers [1]. In turn, cobalt and nickel nanomaterials with their oxides are the potential for use in catalytic systems, magnetic materials, semi-conductor and bio-sensors [2].

Moreover, the colloidal solutions with of nanoparticles of different metal (in particular, copper, silver, molybdenum, etc.) have excellent bactericidal, antiviral, antifungal and antiseptic effects [3], what makes them essential biocide products.

It is nature that to improve the characteristics and properties of solutions with nanoparticle it is necessary to investigate directly the process, which occurs during nanoparticles formation. Namely, the plasma of discharges, which burns between granules used as a source of metal particles in the obtained solutions, should be understudy. The most suitable approach to such investigation is optical emission spectroscopy. On the one hand, this method enables to obtain with sufficient accuracy the main plasma parameters, such as temperature and electron density, which characterise the processes of nanoparticles formation. On the other hand, such technique does not perturb the plasma and cannot affect the properties of the resulting product.

In our previous work the discharge in water between some kinds of metal granules was investigated. In particular, the peculiarities of diagnostic of plasma with admixtures of iron [4] and copper [5] were considered. The present study focuses on the peculiarities of plasma spectroscopy of underwater discharge between molybdenum granules.

The molybdenum material is of practical interest due to its various applications and peculiarities. First of all, molybdenum is an important micronutrient, which provides the nitrogen capture from air atmosphere by bacteria promoting the synthesis of new proteins for plants [6-8]. Therefore, the use of molybdenum in colloidal solutions can significantly improve the viability of plants or their seeds treated with such substances.

In addition, molybdenum can be used in electrocatalytic water splitting accompanied with hydrogen and oxygen evolution reactions [9, 10], which is important for the creation of renewable energy sources. The molybdenum in this application is a potential alternative for compounds on the base of Pt and Ir/Ru noble metals, which are used as efficient water splitting electrocatalysts. In this case Mo-based material, namely molybdenum oxide as a widespread and inexpensive material can be used as the electrocatalyst with high activity and durability both in the hydrogen evolution reaction in the acidic environment [11] and in the oxygen evolution reaction in the alkaline environment [12].

Moreover, it was found in the work [13] that nanoparticles of molybdenum oxides can be synthesised and deposited on the polymer surface during plasma treatment with water anode. Therefore, such compounds based on molybdenum can be used for plasma modification of polymeric materials, which, in turn, are widely used as a substrate for photocatalysts due to its chemical inertness, high durability, inexpensive and readily available, and high ultraviolet resistance [14].

Considering the abovementioned, the main aim of this work is to investigate the possibilities of using of optical emission spectroscopy techniques for the diagnostic of underwater discharge plasma between different metal granules, specifically molybdenum, as well as determination of the key plasma parameters of such discharge, namely, excitation temperature and electron density.

### **EXPERIMENTAL SETUP**

The investigation of underwater discharge plasma between iron granules is carried out directly in the discharge chamber of the installation, specially developed for the synthesis of colloidal substance with metal nanoparticles (see Fig. 1.).

The discharges are ignited by pulses of the generator, which is powered by a single-phase voltage 220 V, between iron granules, immersed into water inside the chamber. The composition of power diodes VD1 and VD2, thyristors VD3 and VD4 and capacity C1 (adjustable from 25 to 650  $\mu$ F) is used as a controlled phase rectifier. Randomly switching of microdischarges between various pairs of granules is realized due to pulse voltage in output of

thyristor VD5. Registration of electrical parameters can be performed by the voltage divider, Rogowski coil and oscilloscope.



Fig. 1. Experimental arrangement for pulsed underwater electrical discharge investigation [15]

The granules, immersed into deionized water, are moving during the discharges, which leads to the changing of discharges position in the volume of the chamber. The observation and registration of radiation were allowed by quartz window, which was installed into the wall of the discharge chamber. Under these conditions, it is not possible to fix the locations of discharges, so the spectral device was placed in front of the window in the mode of continuous registration. It was possible to successful register the radiation of moving discharges when it fell into the area in front of the window.

The registration of emission spectra of underwater discharge plasma at current pulse up to 150 A is provided by Solar LS SDH-IV spectrometer in the spectral range from 440 to 910 nm. The spectral sensitivity (see Fig. 2.) of such device is determined by tungsten band-lamp and is taken into account during spectroscopy treatment.



Fig. 2. Spectral sensitivity of the spectral registering device

The excitation temperature of underwater discharge plasma was determined by Boltzmann plot technique using the emission intensity and spectroscopic data of Mo I spectral lines [16, 17] as follows:

$$ln\left(\frac{I_i\lambda_i}{A_ig_i}\right) = -\frac{E_i}{k_BT},\tag{1}$$

where  $I_i$ ,  $\lambda_i$ ,  $A_i$ ,  $g_i$  and  $E_i$  are emission intensity of the corresponding spectral line, its wavelength, transition probability, statistic weight and energy of upper level, respectively.  $k_B$  is a Boltzmann constant, T is a temperature.

The electron density in this plasma was determined from FWHM (full width at half maximum) of  $H_{\alpha}$  spectral line according to Stark mechanism of this line broadening. The dependence of electron density from FWHM for this line expressed as follows [5]:

$$N_{e}\left[m^{-3}\right] = 10^{23} \times (w_{S}[nm]/1.098)^{1.47135}, \qquad (2)$$

where  $w_s$  is a Stark width of spectral line.

The Voigt function was used for spectral line approximation to determine both the emission intensity and FWHM. The necessity of utilization of this approach is caused by the importance of accounting the instrument function of used spectrometer [18].

#### **RESULTS AND DISCUSSIONS**

The emission spectrum of underwater discharge between molybdenum granules is shown in Fig. 3 (black line). It is clearly observed that such emission is characterised by a certain rise of continuum emission in the blue spectral area. This phenomenon can be caused by various reasons, which were under considering in electric arc discharge free-burning in air atmosphere [17]. In this case, it can be assumed that this emission was caused by formation of molybdenum oxides nanoparticles. This can be confirmed by the results, obtained in [13], where the same phenomenon during synthesis process of such nanoparticles was found. It was found in [13, 17] that the continuum simulated according Planck's law shows reasonable agreement with real obtained spectra. In this regard, the similar simulation of blackbody radiation was carried out in this investigation (see Fig. 3, red line). One can see that distribution of this radiation intensity coincides with continuum emission in the observed spectrum.



Fig. 3. Registered emission spectrum of underwater discharge between molybdenum granules and simulated black-body radiation

In order to account the contribution of this radiation into emission intensity of spectral lines at the next step of spectrum treatment the simulated black-body radiation was deducted from registered spectrum. The obtained real emission spectrum is shown in Fig. 4 (black line).



Fig. 4. Emission spectrum with the deducted black-body radiation and simulated spectrum using data taken from NIST [19]

The emission of Mo I spectral lines was simulated using data taken from NIST [19] to identify these lines in the obtained spectrum (Fig. 4, red dots). One can see, the emission of this underwater discharge plasma consists of predominantly Mo I spectral lines and  $H_{\alpha}$  with triplet of O I 777.1 nm, which is natural for discharges ignited in water.



Fig. 5. Approximation of selected spectral range with essential "background" emission

It was found that emission intensity distribution reconstructed by approximation of 27 peaks fully coincides with radiation in this spectral range (see Fig. 5). It indicates that this "background" emission caused simply by overlapping of spectral lines' contours.

It should be concluded that the spectral range consisting of large number of spectral lines must be approximated with the simultaneous inclusion of each of them. Such approach allows to avoid the presence of false "background emission and, consequently, the overestimating the spectral line intensity, which, in turn, enable to correctly determine the excitation temperature.

As it was mentioned above, the excitation temperature of underwater discharge was determined by Boltzmann plot technique (see Fig. 6) on the base of previously selected Mo I 473.1, 476, 550.6, 553.3, 557 and 603.1 nm spectral lines [16]. The excitation temperature in this case was 12800±1700 K.

However, it should be noted that other spectral lines of molybdenum were observed on the emission spectrum as well. In order to validate the obtained excitation temperature as well as to provide the better accuracy of diagnostic of plasma with molybdenum admixtures the aforementioned lines were additionally used in Boltzmann plot, as it shown in Fig. 7. The excitation temperature, determined by Boltzmann plot technique on the base of previously selected and additionally proposed Mo I 468.8, 470.7, 481.1, 481.9, 483.1, 499.9, 568.9, 572.3 and 575.1 nm spectral lines, was 13600±1200 K.



Fig. 6. Boltzmann plot for plasma of underwater discharge between molybdenum granules on the base of previously selected spectral lines



Fig. 7. Boltzmann plot for plasma of underwater discharge between molybdenum granules on the base of observed Mo I spectral lines

One can see from Fig. 7 that including into consideration of the additional spectral lines of molybdenum leads to a certain increase in the excitation temperature. At the same time, the error of calculation decreased, which indicates the expediency of utilization of aforementioned

spectra lines when determining the excitation temperature in the plasma of underwater discharge between molybdenum granules.

As well as excitation temperature of discharge plasma was determined using emission intensity of Mo I spectral lines in assumption of Boltzmann distribution of energy levels population, the electron density in just this plasma was obtained from FWHM of  $H_{\alpha}$  spectral line in assuming that Stark effect is a dominant broadening mechanism of this line. At this stage of diagnostic, the issue of approximation, mentioned above (see Fig. 5), emerged as well. Namely, it was impossible to achieve the complete coincidence of fitting curve with spectral line contour (experimental dots). It was found that several spectral lines of molybdenum can emitted in this spectral range (Fig. 8, red dots). In this regard, the multiple peak approximation was also used. As a result, the best coincidence of fitting curve with  $H_{\alpha}$  profile was achieved (see Fig. 8).



Fig. 8. Approximation of contour of  $H_{\alpha}$  spectral line

Electron density in this plasma of underwater discharge between molybdenum granules was obtained by eq. 1, in which the Stark width  $w_s$  was equal to Lorentzian width  $w_L$  as a part of Voigt function. The instrumental function was taken into account as a Gaussian width  $w_G$  of Voigt function (see Fig. 8). The electron density determine in this way was  $5 \times 10^{23}$  m<sup>-3</sup>.

It should be noted, the results of measuring the temperature and electron density practically coincide with those obtained for discharge between copper granules [5] at the same experimental condition of the discharge.

#### CONCLUSIONS

The plasma spectral emission of the underwater electric spark discharge between metal granules was investigated. The special attention is paid to peculiarities treatment of emission spectrum radiated by plasma of discharge between molybdenum granules immersed into water.

Optical emission spectroscopy methods are used for diagnostics of such discharge plasma. The Boltzmann plots of metal atom lines' intensities are used to determine the plasma temperature.

Profile of  $H_{\alpha}$  spectral line, exposed to the Stark mechanism of spectral lines' broadening, is used to determine the electron density.

It was clearly observed that emission of plasma with molybdenum admixtures is characterised by a continuum emission in the blue spectral range. It was assumed that the origin of this emission is black-body radiation, which, in turn, caused by radiation of the formed nanoparticles of molybdenum oxides in the underwater discharge.

In addition, it was concluded that it is important to take into account the all significant radiation from the considered spectral range, in particular, all spectral lines which can emitted, in order to correctly determine both the emission intensity of particular spectral line and its width.

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# INFLUENCE OF PLASMA FLOW ON THE VELOCITY OF FEEDSTOCK POWDER DURING PLASMA SPRAY

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#### ABSTRACT

Plasma spray technology is widely used in manufacturing industry for development of numerous protective coatings. The coatings applied to mechanical surfaces exhibit enhanced corrosion resistance and hardness. During the plasma coating spray process the quality of the coatings can be widely controlled by selecting proper spraying conditions. One of the main control parameters is the power of the plasma torch. It directly affects the speed and temperature of the plasma jet, which in turn affects the velocity of the particles that are being accelerated towards the sample inside the plasma jet. Therefore, the aim of this research is to investigate the influence of the plasma torch power on plasma jet temperature and velocity. Also, to determine the velocity of in-flight Al<sub>2</sub>O<sub>3</sub> particles inside the plasma jet at various torch powers. The power of the plasma torch was increased from 28.0 kW to 41.8 kW, resulting in temperature increase from 3100°C to 3700°C, and speed from 970 m/s to 1160 m/s in plasma jet. Velocity of the in-flight Al<sub>2</sub>O<sub>3</sub> particles inside the plasma jet. Velocity of the particles inside the plasma jet increased from 250 m/s to 600 m/s with the increase of torch power.

Keywords: Plasma spray, torch power, plasma flow, particle velocity

### **INTRODUCTION**

Atmospheric plasma spray is a flexible, industry-scalable, and cost-effective manufacturing processing technique. This technique has been extensively utilized for depositing metallic and ceramic coatings to protect the substrates from abrasion, corrosion and thermal shock for more than five decades [1]. The quality of the coating depends on several factors such as plasma temperature and flow rate, the substrate and powders that are being used. Powder composition is especially important, since different materials have different properties and greatly affect the quality of the formed coating, also, adding nanoparticles can significantly improve the properties of coatings [2-5].

One of the main parameter is the plasma torch power. In atmospheric plasma spray feedstock material is injected into the plasma jet. The powders are melted and accelerated towards the substrate, upon impact at the surface, a splat is created when a molten droplet flattens, adheres, and solidifies. Increase in temperature, results in reduction of dynamic viscosity of droplets, and this, together with the higher collision speed of droplets lead to a higher degree of flattening [6]. This splat constitutes the basic building element of the coating, its shape and adherence to the surrounding material having a marked effect on the microstructure. Thus, the in-flight particle characteristics are bound to the overall structure and properties on the sprayed coating. Process control and optimization are essential to fulfill actual application requirements [7-8]. Particle velocity as a function of power was investigated by S. Guessasma [9]. In his work Al<sub>2</sub>O<sub>3</sub>-13%TiO<sub>2</sub> powders were used to measure particle velocity increase by increasing the current of the plasma torch from 350 A to 750 A. It was determined that the average speed of the particles increased from 214 m/s to 322 m/s. Since particle velocity can influence the properties of formed coatings this was investigated by Y. Bai [10]. It was

observed that the velocity of the in-flight particles is directly proportional to the reciprocal of the porosity and structure uniformity of the coatings.

The aim of this research is to investigate the influence of the plasma torch power on plasma jet temperature and velocity and to determine the velocity of in-flight  $Al_2O_3$  particles inside the plasma jet at various torch powers.

## METHODOLOGY

Experiments were carried out using a direct current plasma torch developed at the Lithuanian Energy Institute. Thermal spraying was carried out using a gas mixture of air (flow rate of 4.45 g/s) and hydrogen (flow rate of 0.06 g/s) as plasma gas. Air was also used as a carrier gas for the feedstock powder. Gas flow rates were constant during the experiments.

Conventional Al<sub>2</sub>O<sub>3</sub> powder (MOGUL PC15, purity 99.8%) was used as a feedstock material whose size range is between 63 and 140  $\mu$ m. Powders were injected into plasma gun nozzle (internal diameter of 7 mm). Before the spraying process powders were dried to dispose of any moisture that may have accumulated during the storage of the powders.

The mean temperature of the plasma jet at the exhaust of the plasma torch was calculated from the heat balance corresponding to plasma enthalpy. Detailed description of the methodology of the plasma temperature and velocity calculation is given in [11-12].

The velocity of the in-flight particles was determined using a high-speed camera footage. Several frames of slow-motion footage were analysed using ImageJ picture processing software. In these pictures, the speed was calculated by measuring the travel distance of several particles in plasma jet over a certain period of time.

Three different plasma torch powers were used in this experiment: 28 kW, 35.1 kW, and 41.8 kW. Several measurements were done for each case and mean values are given below.

## **RESULTS AND DISCUSSION**

The temperature and speed of plasma jet for all three torch powers are shown in figure 1. As expected, with an increase in plasma torch power, both the temperature and velocity of plasma jet are increased simultaneously owing to the mechanical and electromagnetic pinching effects on plasma arc. Such effect leads to an increase in particle velocity and a decrease in the dwelling time of the particle in plasma jet inevitably. Therefore, the increase in the heating effect owing to jet temperature increase can only compensate the shortening of dwelling time of particles in plasma jet. Figure 1 shows plasma jet temperature as a function of plasma torch power. With the increase of torch power by 25%, temperature increases by only 6%, from 3100°C to 3300°C, but continuing to increase the power by 49% results in increase of plasma jet temperature by 19% to 3700°C. Since plasma jet velocity is directly proportional to the temperature, same tendencies can be observed. At first the power increase results in only 4% increase in speed, from 970 m/s to 1010 m/s, but further increase, raised plasma jet velocity by 20%, to 1160m/s.



The in-flight particles velocity was determined using footage from a high-speed camera, that was used to capture spraying process in slow-motion at 60000 frames per second. Several frames were captured and particle velocity was calculated using ImageJ software. Two frames used in image analysis of the spraying process is shown in figure 2. The timestamp of first frame is 0.032944 s and for the second one -0.033011 s. Two different particles are highlighted, a smaller, more centrally located red particle and bigger, further away from the centre green particle. In the next frame (fig. 2 b) same two particles are highlighted. The velocities of these two particles were calculated by measuring the distance that was travelled over the fracture of a second between two frames.



Fig. 2. Slow-motion footage frames a)1st frame; b)2nd frame with marked red – smaller more centred and green – bigger, more distant particles

From the image analysis, it is clear that smaller and more centrally aligned red particle is faster. But green particle is slower not only due to its size, but also because it is further away from the plasma jet. Such particles may move so far away from the centre and not even hit the substrate. The red particle is more likely to hit the intended target and form a protective coating. Therefore, in further calculations, only particles that aligned with the plasma jet and were most likely to participate in the coating deposition, were used.

Several image analyses were performed and the mean values of the velocity of in-flight particles for different plasma torch powers are shown in figure 3. The increase of in-flight particle velocity is much greater, than of plasma jet. At first the velocity increased by 44%, from 250 m/s to 360 m/s, continuing to increase the plasma torch power resulted in 140% in particle velocity, to 600 m/s.



Fig. 3. In-flight particle velocity as a function of plasma torch power

## CONCLUSIONS

The increase of plasma torch power from 28 kW to 41.8 kW increased plasma jet temperature by 19%, from 3100°C to 3700°C and plasma jet speed by 20%, from 970 m/s to 1160 m/s. This increase was not linear due to other processes during the plasma spray, such as cooling of the plasma spray equipment. The velocity of the in-flight particles increased by 144%, from 250 m/s to 600 m/s. These results show that plasma torch power is a great way to control the conditions of plasma spraying process in order to obtain favourable results.

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## THERMAL PLASMA TREATMENT OF HAZARDOUS WASTE (REVIEW)

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#### ABSTRACT

As the economy grows and the standard of living improves, the consumption and waste generation increases very fast worldwide. In order to reduce the amount of waste going to landfills, the waste is intensively sorted and prepared for recycling. A part of it is characterized as hazardous materials and adverse effect on humans health.

Several numbers of thermal treatment techniques are well-developed and used. The thermal treatment of hazardous wastes is considered as one of the best methods around the world. However, there exists a plasma treatment technology which considered be as a technology of the future. The plasma treatment at high temperatures provided by thermal plasma torches is the main alternative applied for destruction of hazardous wastes in cases when the traditional combustion methods produce the by-products which can cause harm to human health and environment. The destruction of different types of waste with plasma method, due to its unique properties is characterised as an environmentally friendly process: the destruction degree of hazardous materials in plasma devices reaches up to 99.99% The literature review presented in this paper examines the thermal methods, and reveals their advantages and disadvantages.

Keywords: thermal plasma, solid waste, plasma source, destruction of hazardous waste

### **INTRODUCTION**

The requirement for the air, water and soil quality, as well as hazards emission and its sources localisation annually increases. However, the world's situation on environmental protection and energy efficiency areas does not improve fast enough. Rational utilisation of natural resources and protection of the environment from pollution is still one of the most important tasks of today. Vast amounts of various wastes and harmful substances are accumulated not only in Europe but generally around the world. Pesticides, old tires, various oil and gas industry chemicals, plastics, harmful industrial and domestic waste, obsolete medications and medical waste, toxic substances from energy companies and transport could be identified as the most common hazardous waste [1–4]. Exposure to these substances causes a great risk for nature and humans. In the context of increasing environmental demands, environmental protection problems are being tackled intensively in foreign countries: harmful substances are sorted, recycled, and new waste-free and low-waste technologies are being developed.

According to Eurostat [5], the total amount of waste in 2018 was 101.4 million tonnes. Among these wastes generated in the EU, about 4,3 million tonnes contained hazardous waste, which consisted of other mineral 17.53%, chemical 13.86%, combustion 12.44%, mineral waste from construction and demolition 11.23%, soils 9.51%, discarded vehicles 7.8% [6]. The share of hazardous waste in a total waste generation was below 10.0 % in all of the EU Member States except Estonia and Bulgaria, where it made up 46.9 % and 10.4 %, respectively. The very high share for Estonia was principally due to energy production from shale oil.





Fig. 1. Hazardous waste generated in 2010 and 2018 [5]

## METHODS OF THERMAL TREATMENT

There exist a number of waste management and decontamination methods including mechanical, sorption, chemical, biological, thermal and combined [7]. The most effective and economically attractive for the treatment of hazardous waste is the thermal method. The thermal decontamination is applied to any waste treatment technology that involves high temperatures in the processing. The heat is used to melt or vaporize those chemical contaminants that readily convert from a solid or liquid to a gas fixed carbon(char) and ash. In the presence of heat, all the waste can be oxidized and decomposed to non-hazardous substances.

The main methods of thermal decontamination of wastes are:

I) Low-temperature oxidation. The method's essence is the oxidation of complex or elementary organic compounds employing air or oxygen at a temperature of 150-350 <sup>0</sup>C and a pressure of 2-3 MPa [8]. This method is mainly applicable for cleaning sewage waters. The process takes place due to the high dissolved oxygen concentration.

II) Heterogeneous catalysis. This method is used for decontamination of gaseous waste by reducing the oxidation temperature of the toxic components. With the help of catalysts, the neutralization temperature can be reduced up to 180 - 400 <sup>0</sup>C. It is important to notice that the use of the method of thermal catalytic neutralizers is much narrower than other thermal methods since the maximum working temperature is often 900 <sup>0</sup>C [9]. If the concentration of flammable components in the waste is high, the combustion temperature is also high, and the catalyst may burn off.

III) Pyrolysis. It is the heating and decontamination of materials without air [10]. Usually, the process occurs in the inert atmosphere, e.g., N<sub>2</sub>. In the pyrolysis process, solid, liquid and gaseous products of various compositions are obtained: CO, CO<sub>2</sub>, H<sub>2</sub>, CH<sub>4</sub>, water, bio-oils coal, slags. During the pyrolysis, endothermic and exothermic processes may take place, as well as wet and dry pyrolysis processes may occur. More important is dry pyrolysis, which involves the thermal decomposition of waste, solid and liquid fuel conversion without an oxidizing agent. Dry pyrolysis of the waste results in pyrolysis gas formation with a high

calorific value, liquid products, and solid carbon residue. The quantity and quality of dry pyrolysis products depend on the composition of the waste and the process temperature.

Two types of dry pyrolysis are distinguished depending on temperature:

a) low-temperature pyrolysis, or semi-coking (300  $^{\circ}$ C - 550  $^{\circ}$ C), in which the maximum yield of oil products and solid residue (semi-coke) and the minimum yield of pyrolysis gas with a maximum calorific value [11];

b) high-temperature pyrolysis >850 °C, at which the yield of liquid products and the solid residue is minimal,[12];

IV) Waste gasification. It occurs when air, oxygen, water steam or mixtures are injected into the ambient of combustible waste. In this way, the wastes are heated, partially burned and gasified [13]. A gas generator usually is a vertical shaft in which solid wastes are supplied from the top and a mixture of air or oxygen and water steam from the bottom. Depending on the type of gas being injected, and the flow rate, a different calorific gas is obtained. The recycling of waste is different from the method of flame neutralization (incineration). It provides flammable gases which can be used as energy and technological fuel, and the resulting resin can be used as a chemical raw material.

V) The incineration method is the most versatile and most effective in comparison with others. It is divided into incineration, flame oxidative and flammable non-reactive method. The burning of waste, their ability to self-burn is the simplest and most reliable way to process them. Waste incineration occurs was over  $1230 \ ^{0}C - 1500 \ ^{0}C \ [14,15]$  by injecting air or air/oxygen mixture. The flame-oxidative method is used to neutralize non-combustible material. The heated combustion products are wastes which heat up and oxidized.

The non-reactive method is applied when there is no free oxygen in the reaction chamber. Depending on the final result, the incineration method of decontamination of waste is divided into three other types:

• Incineration of waste when hazardous and noxious substances are produced during the destruction of liquid, solid and gaseous waste;

• Flammability recycling when incineration of waste generates one or more useful substances, e.g., calcined soda, metal powders;

• Incineration-recycling of waste when one of the reagents is repeatedly obtained.

## HAZARDOUS WASTE CATEGORIES

Before managing the waste, it is essential to assess whether a waste is hazardous or not and get the available data about waste composition and properties. This information allows choosing the right way for waste management and decontamination. Treatment technologies based on physical, chemical, and biological principles are currently widely used for decontamination of hazardous materials in the water, soils, and sediments [14]. It is well known that all hazardous waste can be divided into the following categories [15]: physical (explosive, oxidizing, flammable), health (skin and eye irritation, specific target organ toxicity, toxic, carcinogenic, corrosive, infectious, toxic to reproduction, mutagenic, sensitizing), environment (ecotoxic). Waste classification is presented in more detail in [16]. Classification and properties of hazardous waste are given in Table 1.

Hazardous Properties		
HP1	Explosive	
HP2	Oxidising	
HP3	Flammable	
HP4	Irritant — skin irritation and eye damage	
HP5	Specific Target Organ Toxicity (STOT)/Aspiration Toxicity	
HP6	Acute Toxicity	
HP7	Carcinogenic	
HP8	Corrosive	
HP9	Infectious	
HP10	Toxic for reproduction	
HP11	Mutagenic	
HP12	Release of an acute toxic gas	
HP13	Sensitising	
HP14	Ecotoxic	
HP15	Waste capable of exhibiting a hazardous property listed above not directly displayed by the original waste	

Table 1. Classification and properties of hazardous waste [16]

Sufficient information about the hazardous substances in the bulk waste should be provided before applying any treatment method.

### THERMAL PLASMA PROCESSING

One of the most important problems in the processing of hazardous waste is chlorineorganic waste disposal [17]. The amount of such waste exceeds millions of tonnes. These include expired products made of chlororganic polymers, spent chlorine organic (including toxic additives), dielectrics (multi-chlorine biphenyls) that have fallen into disrepair waste, chlorine-organic production, etc. Storage of chlorine-organic waste at landfills is dangerous because biological methods cannot decompose such type of waste. The possibility of oxidizing many of them are oxygenated by the sun secondary toxic products. The substantial amounts containing organic combination of Cl, F, P, Hg have been able to decompose to toxic components: the storage of them seems to be one of the most important hazards. The plasma method is useful for the destruction of the toxic materials when the traditional combustion causes harm to humans and the environment or when the composition of hazardous substances can not be identified. By achieving gas temperature over 3000 - 3500 <sup>0</sup>C [18], molecules of hazardous substances decay to atoms, radicals, electrons and ions so that it appears the ability to obtain a simple combination of harmless chemicals. In many cases the DC arc plasma torch (PT) is used for heating air, nitrogen, argon or their mixtures up to 6000 K. The gas of such high temperature are used for destruction hazardous waste. High-temperature reactors for that aim usually are being connected to the PT. The plasma jet-reactor (Fig. 2.) could be applied as a mean for the treatment of solid, liquid and gaseous waste.



Fig. 2. The schematic presentation of a plasma system for the destruction of hazardous substances suggested by Alter NRG Inc. [18]

This thermal neutral plasma process is environmentally friendly and allows materials to be restored and at the same time, extract the synthesis gas contained in the initial product. In this process, the metals and ceramic substances are melted, plastic (mostly polyethylene) is melted, evaporated and thermally decomposed with the following external condensation in a specific device or collected in the form of synthesis gas. The resulting products of the process are synthesis gas, recovered metals and vitrificated glass of very high quality which can be directly used to benefit in various industries.

The plasma processing of hazardous waste requires in-deep knowledge on gas dynamics and heat transfer in channels with high-temperature gas flows. Distribution of velocities, temperatures, and fluctuations in high-temperature jets and flows should be measured and analyzed. The whole burning cycle may be automatically controlled with an electronic panel, resulting in perfect incineration along with environmental protection.

The high degree of destruction of hazardous waste (99,99%) and completely new approach in the industrial manufacture applicable to large amounts and all kinds of waste products. The main advantages of the plasma method: a) the possibility to burn any waste product with large moisture content, b) there is the ability for automatic control of the burning procedure according to the feed rate, c) exhaust gas emissions are very low, d) the burning stages are controlled in the main control panel.

In plasma systems, electricity is used to form an electric arc with the temperature of up to 10000 K [19]. Plasma is generated using a plasma torch from any plasma-forming gases. In these plants, waste is heated to 1550–2000 K or more. As a result, all hazardous compounds are destroyed, and the inorganic part of the waste is converted into neutral slag and reduced metals. The thermal plasma treatment exists effectively in two forms: pyrolysis [20] and gasification [21]. Pyrolysis in plasma ambient appears as a similar process to the classical pyrolysis. During plasma decomposition of wastes containing organic substances with the lack or absence of an oxidizing agent, a solid carbon-like residue and pyrolysis gas containing high-boiling resinous substances are formed. The calorific value of such gas is about 8-18 MJ/m<sup>3</sup>.

During the thermal plasma decomposition of waste, oxidative pyrolysis causes their partial burning in direct contact with the gaseous products of fuel combustion. Gaseous waste decomposition products are mixed with fuel combustion products or part of the waste, so they have lower heat of combustion at the elevated temperature at the reactor's outlet. Such a gas mixture is then burned in conventional combustion devices for producing energy. During the oxidative pyrolysis, a solid carbonaceous residue (coke) is formed which can be used as a solid fuel or for other purposes.

The researchers of [22] demonstrated that the pyrolysis process could reduce the yield of hazardous sludge. Several stages occurred inside of the fixed-bed pyrolysis reactor are as follows:

- heating process inside the reactor;
- liquid content evaporation;
- the thermochemical conversion.

The results showed that the gasification process effectively reduces the volume of hazardous sludge up to 40% of the total sludge mass. The reduced mass contains moisture and volatile carbon which are decomposed by the thermal plasma process.

During plasma gasification process waste containing organic substances in the presence of oxidizing agent (air, oxygen, water vapor, carbon dioxide or a mixture thereof) with a flow rate below stoichiometric, the production of generator gas (synthesis gas) and a solid or molten mineral product is available.

Studying the practicality of plasma gasification of municipal solid and hazardous waste [23] carbonaceous waste deposited in the oil and gas industry it has been stated that the efficiency of plasma gasification, the plant efficiency and other performance parameters are discretic by using the overall thermochemical model. Performing the studies on various waste mixtures with different plasma forming gasses and combining air with either steam or oxygen has been found that for a waste mix comprising 50% of municipal solid waste and 50% of petroleum hazardous waste the attained plant efficiency is 24.3% for the pure air as plasma generation gas. This value can reach as high as 41.1% when pure oxygen is used as plasma gas instead.

The innovative technology for plasma destruction of solid waste, such as sewage sludge or other waste containing heavy metals has been suggested by researchers of Lithuanian Energy Institute [24,25]. It consists of two chambers with single or two different plasma torches that create the appropriate conditions for effective and uniform burning of household and pathological waste products. In the first chamber, controllable burning of electric arc takes place at a temperature of 2500 °K, while in the second chamber the off-gases are re-burned with the addition of excess air at a temperature of 3700°K. Schematic structure show on (Fig. 3).





### CONCLUSIONS

Waste management poses a significant problem for current and future generations. In addition to simple accumulation and space issues, the presence of hazardous and toxic materials poses environmental and health problems as well. The introduction of thermal plasma arc technology serves to alleviate these problems. By decreasing the overall mass of waste materials and rendering such pollutants as heavy metals inert, this technology can prove to subside further damaging effects to the Earth. The generation of syngas also makes plasma furnace technology an energy-efficient alternative to traditional methods of garbage disposal. With the right calculations, the process can even become commercially profitable within the energy sector. With these advantages and the ability to process waste in different forms; be it solid, liquid, or bio-organic matter, it is reasonable to consider this technology the future of waste management and disposal.

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# THERMAL TREATMENT OF DIGESTED SEAWEED AND PRODUCTS ANALYSIS

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#### **OVERVIEW**

In recent decades, higher and higher energy consumption leads to depleting fossil fuels and reducing crude petroleum resources. As an alternative, recovered energy from biomass could be used. Plenty of different thermochemical reactions have been processed for converting biomass into higher added value energy products [1]. Pyrolysis is one of the most preferable because it is efficient and environmentally friendly [2]. Moreover, this biomass conversion into energy products may solve some environmental problems. The ongoing eutrophication processes caused by macroalgae ecological and social consequences are critical issues of water pools ecosystem and environment. The combined system of anaerobic digestion and thermal treatment could offer many opportunities for the Baltic Sea Region to recycle low-quality resources and wastes in renewable, high-quality biofuels. Anaerobic digestion may offer great solution for primary biomass treatment, gathering biomethane, and generating digestate. In the best case, collected digestate after anaerobic digestion may be used for the field's fertilization purposes, contributing to creating a circular economy. However, the seaweed tends to absorb nutrients, minerals, and pollutants, which are filled with heavy metals. For that reason, seaweed and digested seaweed is not an appropriate solution, and other utilization pathways must be explored. Also, the efficiency of the anaerobic digestion could be increased by mixing the feedstock with additional substrate, such as sewage sludge [3].

In order to generate more energy products, digested seaweed could be supplied for thermal treatment under a pyrolysis atmosphere. Three different higher added value energy products (liquid, gas, and char) would be produced in that case. The use of pyrolysis products shows undisclosed thermal treatment abilities as an alternative for fossil fuel consumption. Thermal biomass waste utilization could be a great opportunity for energy product generation and contribution to creating of circular economy.

### **METHODS**

The feedstock (macroalgae) was collected in Melnrage beach, which is a part of Klaipeda city in the north of the Curonian Lagoon confluence with the Baltic Sea. The seaweed has a high amount of sand, which is necessary to wash. Washed seaweeds were dried in accordance with ISO 579 standard and used for further experiments.

In order to analyse the thermal characteristics of selected samples, Netzsch Jupiter F3 (Germany) thermal gravimetric analyser (TGA) has been used. The main parameters of these experiments are depicted in Table 1. Moreover, to evaluate the gaseous products' composition, which emits during the pyrolysis experiments, TGA coupled with Fourier transform infrared spectroscopy analyzer (FTIR, Bruker) and gas chromatography with quadrupole mass spectrometer detector (GC/MS, Agilent 7890A).

Parameter	Value
Carrier gas	Nitrogen (N <sub>2</sub> )
Carrier gas flow, ml/min	60
Maximum temperature, °C	900
Heating rate, °C/min	30
Amount of sample, mg	10-15

Table 1. The main parameters of TGA

The FTIR analyser scan times are 32. The wavelength interval ranges between  $650 - 4500 \text{ cm}^{-1}$ . For all experiments used the LN-MCT (liquid nitrogen) detector with a resolution of 4 cm<sup>-1</sup>. One of the most important part of the GC/MS experiments are the column's type and parameters. For these experiments used a universal HP-5MS column with (5%-Phenyl)-methylpolysiloxane filling. The column's length is 30 m, while the outer and inner diameters are 250 µm and 0.25 µm, respectively. The mass scanning diapason ranges from 13 to 600 m/z.

### RESULTS

The thermal analysis in the micro-scale was processed using the TGA-DTG system. The results showed that all three types of biomass have two decomposition peaks. The first peak (X<sub>1</sub> and X<sub>2</sub> in Fig. 1 A) occurred around 310 - 350 °C and could be assigned to cellulose and hemicellulose thermal decomposition, which could be found in the feedstock. The second peak (X<sub>3</sub>) appeared at 700 - 720 °C and belonged to lignin thermal decomposition. Cellulose and hemicellulose tend to start depolymerization reactions and form monomeric structures around 300 °C [4]. The main thermal degradation of lignin could be observed around 700 °C, tending to the formation of aromatic hydrocarbons and heavier structures [5]. The results of thermal analysis are presented in Fig. 1.



Fig. 1. Thermal analysis TGA (A) and DTG (B) of seaweed, sewage sludge, and digestate

The combination of TGA and FTIR systems could provide data about the main fraction of functional groups in the volatile matter. The results are depicted in Fig. 2. All three samples showed almost similar results. The main functional groups around 300 °C are the C=O group (2300 cm<sup>-1</sup>) which shows typical CO<sub>2</sub> compound, and carbonyl C=O group (1700 cm<sup>-1</sup>). In the sewage sludge and digestate samples could be occurred valence oscillations around 3000 cm<sup>-1</sup>. It shows the presence of the aromatic and aliphatic C-H group. In seaweed samples, two sharp peaks occur at 1300 and 1500 cm<sup>-1</sup>, which shows the N-O group present. Around 700 °C significant peaks are not detected. Only one curve, around 2300 cm<sup>-1</sup> shows C=O (CO<sub>2</sub>) present.



Fig. 2. FTIR analysis of selected feedstocks

The combined system of TGA and GC/MS could provide data about compounds in the volatile matter. Also, the comparison between FTIR and GC/Ms could lead to an exact compound agreement. The results are presented in Fig. 3. The main compounds in the seaweed, sewage sludge, and digestate volatile matter are CO2 (11, 48, and 39 %), respectively, acetic acid, polycyclic aromatic hydrocarbons, and alcohols. Distinctness could be occurred with a seaweed sample, where furfural presence was detected. It reaches 7 % of the total volatile matter composition. Some methane in all samples was also detected. All differences between the products could be explained by the different nature and composition of the feedstock.


# CONCLUSIONS

This study investigated thermal degradation of the seaweed, sewage sludge, and digestate samples. All samples decomposed in two stages. The first one (around 300 °C) belongs to cellulose and hemicellulose thermal decomposition, and the second one (around 700 °C) could be assigned to lignin thermal degradation. FTIR analysis of the selected sample showed the main functional groups in the volatile matter, which are C=O, C-H, and N-O. The main compounds analysed using GC/MS in the volatile matter are CO2, acetic acid, polycyclic aromatic hydrocarbons, and alcohols. According to this investigation, the seaweed and its substrates are potential feedstock for higher added-value product generation. After some additional reactions, these products could be used as transportation fuel, contributing to the circular economy's creation.

Keywords: Thermal treatment; Pyrolysis; Macroalgae; Biomass-conversion; Waste utilization

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# COLD PLASMA TREATMENT EFFECT ON WILD PLANTS SEEDS

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#### ABSTRACT

This study aimed to evaluate the effect of cold plasma (CP) treatment on the seed's germination of such wild field plant species as *Thalictrum minus, Centaurea jacea, Agrimonia eupatoria, Gentiana crusciata,* and *Primula veris.* The results demonstrate that pre-sowing treatment of seeds with cold plasma improved the kinetic parameters of germination of *T. minus* with a 5-fold increase in the number of germinated seeds after 1 minute of treatment. Likewise, there is a tendency towards an increase in the final percentage of germination of the treated *A. eupatoria* seeds. Besides, the results revealed a trend towards an overall growth of the median germination time, which may indicate a slowdown in the germination rate of seedlings. Thus, the obtained data suggest that the treatment of seeds with cold plasma can potentially have a positive effect on the number of germinated seeds of various species of field plants. For species such as *P.veris* and *G.cruscia*, the pre-sowing treatment of seeds with cold plasma did not have any significant effect.

Keywords: cold plasma, wild plants seeds, pre-sowing treatment, germination, Festuco-Brometea

# **INTRODUCTION**

Many studies have shown that the successful meadows restoration and creation of species-rich grasslands are often seed-limited. Sprouting of wild meadows plants' seeds is quite different, which leads to the rare usage of some species seeds. Seeds of some wild plants germinate only after stratification at low temperatures in next season, others germinate in spring with sufficient natural light and temperature. Nevertheless, the regional biodiversity can be preserved only when various types of seeds dormancy of plants of local provenance are used in meadows sowing and restoration projects [4]. The regional plant seeds are often considered the most suitable seed source, reproducing flowering meadows, because they are adapted to the local environmental conditions and improvement.

In this study we are seeking to answer the question, how stressor, such as cold plasma (CP) affects germination of wild plant species *Agrimonia eupatoria*, *Centaurea jacea*, *Gentiana crusciata*, *Primula veris* and *Thalictrum minus* seeds from *Festuco-Brometea* class meadows, which are an endangered type of semi-natural grasslands in Europe. According to ISTA rules, *P. veris* germinates very irregularly over a long period, cooling period is required. *A. eupatoria*, *C. jacea*, *T. minus* germinates rapidly. Fresh seeds of *G. crustiata* listed in Red book of Lithuania, germinates rapidly, but seeds for later collection need to be stratified or vernalized [7]. The cold plasma method has been intensively explored in the last several decades. Many studies concluded that CP improves seed germination and yield of various crops [9] and cultural plants seeds production [1, 3, 10, 11]. However, so far, only a few studies have been published

on the effects of CP on wild plants seed production. Germination tests *in vitro* of red clover cultivar 'Vyčiai' (*Trifolium pratense*) revealed that CP treatments increased germination rate up to 24%, stimulated growth, and induced changes in the amount of major isoflavones in leaves. This effect correlated with changes in the balance of seed phytohormones: a decreased amount of abscisic acid and an increased gibberellin/abscisic acid ratio stimulated root growth and root nodulation [8]. It shows the possibility that wild plants seeds germination stimulation with CP can have an appropriate effect, and more studies in this field are required.

# METHODOLOGY

# Seeds collecting and storing

Wild plants seeds of *Thalictrum minus*, *Centaurea jacea*, *Gentiana crusciata*, *Primula veris 1*, and *Agrimonia eupatoria* species were collected 2019 in the *Festuco-Brometea* plants class meadow at Bradeliškės (54.82638, 24.949936 (WGS)), Vilnius district, Lithuania. *Primula veris 2* was collected in 2018 at Sibirka (54.644926, 24.896934 (WGS)), Trakai district, Lithuania. All seeds were stored at 18°C in paper bags under dry conditions in the dark for three months. The permission to collect the species seeds from Red book of Lithuania was issued by the Lithuanian Environmental Protection Agency (EPA).

#### Seed treatment with cold plasma

Seeds of wild plants were treated with cold plasma in November 2019. The treatment was conducted at the Faculty of Natural Sciences, Vytautas Magnus University.

Pre-sowing plasma treatment of seeds was carried out using an atmospheric pressure scalable dielectric barrier discharge (DBD) device, produced in Kyushu University, Japan, with a homogeneous treatment area of  $4 \times 4.38$  cm (Fig.1), described in more detail elsewhere [3]. An electrical discharge was generated between wire electrodes separated by an insulating ceramic dielectric layer. On a glass sample holder underneath the electrode, intact seeds were laid out in a single layer in a homogeneous zone. The discharge voltage, current, and power density were 7.0 kV, 0.2 A, and 3.1 W/cm<sup>2</sup>, respectively. The distance between the seed surface and the electrode was 5 mm. Seed treatment was carried out at room temperature, atmospheric pressure, and relative humidity of air 50-60%.

Seeds were exposed to CP for 1, 2, and 3 min (CP1, CP2, and CP3 experimental groups). The control group did not receive the treatment. The experiment was replicated 3 times, with 30 seeds per replicate.





The germination results of each replicate were analysed using the application of Richards' function [5] for the analysis of germinating seed population. The indices of germination kinetics: Vi (%) – the final germination percentage indicating seed viability, Me (days) – the median germination time (t50%) indicating the germination halftime of a seed lot or germination rate, Qu (days) – the quartile deviation indicating the dispersion of germination time in a seed lot (half of the seeds with an average growth time germinated in the range Me±Qu) were calculated for control and treated groups.

## Seedling growing conditions

4 days after CP treatment, seeds and control group were sown to vegetation pots with turf in a greenhouse at Lithuanian Research Centre for Agriculture and Forestry, Institute of Agriculture, Department of Grass Breeding in  $+20^{\circ}$ C temperature for 25 days with natural day and night light period. Pots were watered twice a week. Seedlings number was counted each day.

# Statistical analysis

The results were statistically analysed using the software Statistica 10 by TIBCO Software. The analysis was primarily aimed at comparing parameters in control, and cold plasma treated groups in pairs. Means of various parameters between the control and treatment groups were compared using Student's t-tests for independent samples. The differences were assumed as statistically significant at  $p \le 0.05$ .

# **RESULTS AND DISCUSSIONS**

#### **Effects on germination**

The results of germination tests for the control and treated seeds are presented in Table 1.

				r					
	Thalictrum minus		Centaurea jacea			Agrimonia eupatoria			
	V(%)	Me	Qu	$V_i(\%)$	Me	Qu	V <sub>i</sub> (%)	Me	Qu (days)
		(days)	(days)		(days)	(days)		(days)	-
Control	3.3±1.9	10.8±5.5	0.1±0.1	21.1±6.2	5.0±1.0	$0.0\pm0.0$	12.2±10.6	9.8±5.3	0.1±0.1
CP1	16.3±1.9*	15.1±0.8	1.6±0.4*	28.9±6.2	8.0±1.0	1.3±0.4*	$28.9 \pm 4.8$	15.9±1.2	2.0±0.3*
CP2	$12.2 \pm 4.0$	15.1±1.1	0.3±0.1	18.9±2.9	7.3±0.9	0.2±0.1	$18.9 \pm 2.9$	15.9±1.3	0.3±0.0*
CP3	$11.1 \pm 4.0$	11.7±1.1	$0.2\pm0.0$	18.9±1.1	8.1±0.9	0.1±0.0*	36.7±3.3	18.1±0.4	0.3±0.1*

 Table 1. Indices of germination kinetics of seeds calculated from Richards plots

Vi, the final germination percentage; Me, the median germination time; Qu, the quartile deviation; Mean values  $\pm$  standard error of mean are presented (n = 3 replicates, 30 seeds in one replicate).

\*Significantly different from the control group ( $p \le 0.05$ ).

The obtained results show that cold plasma has a general tendency to increase the number of germinated seeds of such analysed species of wild plants as *T. minus*, *C. jacea*, and *A. eupatoria*. Nevertheless, the only statistically significant positive effect of treatment was recorded only after 1-minute treatment with cold plasma of *T. minus* seeds, where the total number of germinated seeds surpassed control by 5-folds.

Cold plasma treatment did not have a significant effect on seed germination rate (Me), only a common trend of slowing germination rate has been observed in all plant species.

Increase in quartile deviation (Qu) in CP1 group of *T. minus* by 16-folds and in CP1 and CP3 groups of *C.jacea* and *A.eupatoria*, by 13, 2, 20 and 3-folds respectively, shows biger disperion of germination time in treated seeds compared to the control whose seeds have germinated more uniformly.

For species such as *P.veris* and *G. crusciata*, the pre-sowing treatment of seeds with cold plasma did not have any significant effect.

# CONCLUSIONS

According to the obtained results, pre-sowing seeds treatment with cold plasma can potentially have a positive impact on the number of germinated seeds of some species of wild plants, which was especially noticeable after treatment seeds of the *T. minus* species. Moreover, acquired results suggest that the effect of cold plasma on analysed species of plants is not differ much among most of the species. Thus, future studies of this presowing seeds stressor could potentially be used for plant remediation of natural sites.

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# PRELIMINARY INVESTIGATIONS OF WATER INJECTION IMPACT ON VAPOUR FROM FLUE GASES CONDENSATION IN A MODEL OF A VERTICAL CONDENSING HEAT EXCHANGER

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#### ABSTRACT

Many opportunities for cost savings are being missed in the industry today because large amounts of waste heat are not being recovered. For the purpose of waste heat recovery, flue gas condensers (condensing heat exchangers) could be applied in many boiler plants. However, the cost of exhaust gas condensers is rather high, and therefore it is important to evaluate carefully the thermal and hydrodynamic processes that take place in these heat exchangers in order to make the right designing decisions. Although the general principles for condensing heat exchangers design are known rather well, this is not the case for flue gas condensers. The literature review has revealed that there are many investigations related to pure vapour condensation. However, investigations of water vapour condensation from flue gases are mostly orientated to the determination of the average heat transfer. Local parameters of the condensation process are not investigated in detail and thus it is not possible to perform optimisation of such type of exchangers. Therefore, this paper presents preliminary investigations of water vapour condensation from biofuel flue gases in a model of a vertical condensing heat exchanger. The paper discusses the results obtained while investigating turbulent flow regimes in flue gases when no water is injected into the flue gases flow and when a certain amount of water is injected but it flows on the wall of the condensing heat exchanger. For the investigated flow regimes when water is injected, in comparison to the case when water is not injected, the changes in temperature distribution are significant from the initial part of the model up to length to diameter ratio  $x/d \approx 70-100$ . At larger x/d, the temperature variations with and without water injections are very similar.

Keywords: biofuel flue gases, vertical condensing heat exchanger, condensing heat-mass transfer, water injection

#### **INTRODUCTION**

The efficiency of heat production is one of the most relevant issues that arise when designing heat production equipment, finding solutions for operating the equipment, and optimizing it. Maximum use of waste heat is one of the features of sustainable energy. Recovered heat increases the efficiency of the plant and thus reduces CO<sub>2</sub> emissions per final amount of the produced heat. In boiler plants, the maximum waste heat potential is observed in flue gases. To prevent corrosion of the surfaces of boilers, the flue gases from the boilers are exhausted at a temperature higher than 150 °C [1]. Flue gas condensers (condensing economizers) are the most popular and advanced solutions for heat recovery from flue gases. In an economizer, flue gases release the heat, cool down to a temperature below the dew point temperature, and the water vapour in the flue gases starts to condensate. These processes highlight two purposes of condensing economizers: to efficiently cool flue gases; and recover the maximum amount of latent heat. In the first case, cooling and moistening systems are installed. In the second case, the issue of used low temperatures is addressed. During the condensation process, an additional amount of heat is generated and can be used to heat the return water from a district heating network or in technological processes. Due to this, condensing economizers can be installed in boiler plants in various connection schemes in order to maximize the utilization of existing low-temperature energy flows [1]. Even heat pumps are installed to increase the usage potential of low temperature heat flows [2, 3].

There are a lot of experimental and theoretical studies devoted to the condensation of water vapour in pipes with a high water vapour content (90–100%, vol.) and a relatively small portion of non-condensable gases [4, 5]. Paper [4] presents a pure vapour condensation model of a vertical condensing tube, the results of which are compared with results of experimental investigations done by others authors. These results reflect the tendencies of local heat flux changes and show the distribution of the heat transfer coefficient along the tube. As the portion of non-condensable gases increases, heat transfer deteriorates.

In the case of flue gas (smoke), the situation is the opposite: the content of water vapour is relatively small (~ 10-25 % vol.) and the portion of non-condensable gases is high, and thus composes the bulk flow. For the design and economy analysis of a flue gas condenser, classical heat exchanger design methods are deficient in the condensing part. In [1] the designed 7.5 m length model of a flue gas condenser consisted of counter-cross flow U-shaped stainless steel tube bundles. The non-condensing part and the condensing part of the heat exchanger were examined separately because in the non-condensing part only heat transfer was efficient while in the condensing part heat and mass transfer was efficient. The results with such a condenser showed that condensation processes started at the end of the flue gas condenser, approx. 6 m. from the inlet of flue gases.

In [6], the condensation of wet flue gases obtained when incinerating natural gas in a boiler was studied experimentally in a vertical pipe of length to diameter ratio  $x/d \approx 79$  and in a Reynolds number range from 2300 to 5000. The results showed that the condensable gas (moisture) existing in the flue gases enhanced the total heat transfer up to two times in comparison with dry air. The wall temperature was also an important factor, which had a considerable effect on the condensation rate and heat transfer.

In [7], a vapour-air mixture was simulated as wet flue gases to provide an analysis of thermal fields and heat and mass transfer in a vertical pipe of  $x/d \approx 70$  and within Re numbers from  $\approx 3000$  to  $\approx 6000$ . The inlet gases mixture temperature was about 60 °C and the cooling water temperature was 20 °C. The volumetric water vapour fraction in the gases mixture was approx. 1 % and 17 %. The obtained results showed that the pipe wall temperature in the case of vapour condensation remained higher by 10–15 °C along the test section compared to that without the condensation phenomenon. The authors also concluded that the heat transfer was influenced by water quantity in the gases mixture. During the experiments, up to 30 % of water vapour was condensed and this led to a substantial increase on the total heat transfer. Other theoretical and experimental investigations also revealed that condensation had a significant impact on heat transfer [8, 9].

An investigation of simulated flue gases condensation with an inlet water vapour mass fraction from 3 to 12 % and Reynolds number from 4600 and 14000 in a vertical short pipe (x/d  $\approx$  32) was presented in [10]. The test section was operating in a counter flow arrangement: cooling water was supplied from the lower part of the test section to the inner pipe and a mixture of hot air and water vapour was supplied in the space between the inner and the outer pipes. It was concluded that in the case of a low inlet water vapour fraction, rough and suction effects were the major factors influencing heat transfer. The measured condenser pipe wall temperature was increasing along the pipe for all investigated Re numbers. For the lowest Re numbers (4600, 6400), the smallest temperature increase was determined along the pipe, i.e. about 2.5–3 °C, and for the highest Re number ( $\approx$  12300), the wall temperature increase along the pipe was ~ 4–5 °C. The heat transfer through condensation was under greater influence when the Re number and the inlet vapour mass fraction were increased.

In conclusion, this literature review has shown that the condensation phenomenon is mostly investigated in short test sections and, in most cases, using simulation of flue gases at relatively

low Reynolds numbers. The purpose of the preliminary investigations presented in this paper is to present temperature distributions in the case of water vapour condensation from biofuel flue gases in a model of a vertical condensing heat exchanger for turbulent flow regimes when no water is injected and when water is injected and flows onto the tube wall of the modelled condensing heat exchanger. Such regimes correspond to real operation conditions in a heat exchangers used in industry boiler plants.

# METHODOLOGY

## **Experimental setup**

The experimental setup with the test section is presented in Fig. 1. Flue gases were generated by incinerating wood pallets in a Kostrzewa boiler (Poland). The boiler is classified as class 3 (according to EN 303-5:2012 standard) with power adjustment range from 50 to 100 %. The boiler was additionally equipped with a flue gas moistening system in order to increase the humidity of the combustion products.



Fig. 1. The experimental setup with the test section

The flow rate of flue gases through the test section was adjusted by flow control dampers and a flue gases exhaust fan, which was controlled by a frequency converter. The required flue gases flow was directed to the test section, and the excess flue gases flow was directed to the chimney directly through the bypass. A flow meter and a humidity/temperature transmitter (the measurement points) were installed before the water injection chamber. Temperature and relative humidity were measured using an electronic humidity/temperature transmitter Kimo C310. The accuracy for RH<sub>in</sub> measurement is  $\pm 0.88$  % and for temperature  $\pm 0.3$  %. The flow rate of flue gases was measured using a bellmouth with installed Pitot-Prandtl tubes connected to a differential pressure meter. The water injection chamber was designed in such a way that the injected water forms a water film and flows down the calorimetric tube. Water used for the injection into the calorimetric tube was distilled water supplied from a graduated water tank.

The test section is a model of an industrial condensing heat exchanger with operating conditions close to conditions in one channel of the heat exchanger. Flue gases flows through the inner calorimetric tube (inner  $\emptyset = 0.034$  m, length  $x \approx 5.8$  m and  $x/d \approx 171$ ) of the model. The flow of flue gases is cooled by water. The flow of water is annular around the calorimetric tube and surrounded by the outer tube (inner  $\emptyset = 0.108$  m,  $x \approx 5.8$  m). Cooling water is supplied by a pump into the lower part of the model. Water flows out from the top of the test section and is directed to a heat exchanger (air-water) where it is cooled down and returns back to the water tank (0.2 m<sup>3</sup>). The cooling water flow rate is measured by a beaker and a stopwatch at the outlet hose from the air-water heat exchanger.

The model is equipped with calibrated Chromel–Copel thermocouples for temperature measurements (accuracy  $\pm 0.3$  %):

- 20 thermocouples installed in the centre of the calorimetric pipe along the length of the tube (distances between thermocouples 0.28 m);
- 20 thermocouples installed at the inner wall of the calorimetric pipe (i.e. from the flue gases side) along the length of the pipe (distances between thermocouples 0.28 m);
- 10 thermocouples installed between the inner and the outer pipes to measure the cooling water temperature along the length in the space between pipes (distances between thermocouples 0.56 m).

All thermocouple data were collected using the automated data acquisition system Keithley. In the model, the elbow is mounted below the heat exchanger to change the direction of flue gases to the chimney. Drainage is installed at the lowest point of the elbow for condensate and injected water collection. The condensate collection tank is graduated.

All ducts and the test section are isolated by 5 cm insulation.

#### **Data processing**

During the experiments, all the data were obtained for steady state conditions. The flue gases velocity (m/s) in the bellmouth was calculated using the equation:

$$w = \sqrt{\frac{2\Delta p_d}{\rho}},\tag{1}$$

where  $\Delta p_d$  is dynamic pressure, Pa,  $\rho$  is flue gases inlet density, kg/m<sup>3</sup> (based on the flue gases inlet temperature t<sub>in</sub>).

The volumetric inlet flow rate  $(m^3/s)$  of the flue gases into the calorimetric tube is equal to:

$$G_{in} = \mathbf{w} \cdot \mathbf{a},\tag{2}$$

where *a* is the minimal cross section area of the bellmouth,  $m^2$ .

The inlet flue gases velocity (m/s) in the calorimetric tube was calculated using the equation:

$$w_{in} = w \cdot \frac{a}{a_{in}},\tag{3}$$

where  $a_{in}$  is the internal cross section area of the calorimetric tube, m<sup>2</sup>. Other parameters are the same as in equations 1 and 2.

The flue gases Reynolds number at the inlet into the calorimetric tube was calculated as:

$$Re_{in} = \frac{w_{in} \cdot d}{v_{in}},\tag{4}$$

where d is the internal diameter of the calorimetric tube, m,  $v_{in}$  is the kinematic viscosity of flue gas, m<sup>2</sup>/s. Other parameters are the same as in equations above.

Temperatures in the test section were measured periodically until steady state conditions were reached. At this point, time, injected water flow, and collected water flow rate were determined. The condensate flow rate was calculated as:

$$\dot{m}_c = \dot{m}_{collected} - \dot{m}_{inj},\tag{5}$$

where  $\dot{m}_{collected}$  is the mass flow rate of collected water in the condensate collection tank, kg/s,  $\dot{m}_{ini}$  is the mass flow rate of injected water, kg/s.

The heat balance was calculated to evaluate the correctness of the experiment. The heat quantity (kW) obtained by cooling water was calculated as:

$$Q_{w} = \dot{m} \cdot \left( c_{pw_{out}} \cdot t_{w_{out}} - c_{pw_{in}} \cdot t_{w_{in}} \right), \tag{6}$$

where  $\dot{m}$  is the mass flow rate of cooling water, kg/s,  $c_{pw out, in}$  is the specific heat of water at the outlet and inlet temperatures, respectively, kJ/kg °C,  $t_{w in, out}$  is cooling water at the inlet and outlet temperatures, respectively, °C.

The heat quantity (kW) from flue gases excluding the quantity used for the heating of injected water:

$$Q_{b} = \dot{m}_{g}(c_{pg_{in}} \cdot t_{g in} - c_{pg_{out}} \cdot t_{g out}) + r \cdot \dot{m}_{c} - \dot{m}_{inj}(c_{p inj_{out}} \cdot t_{inj out} - c_{p inj_{in}} \cdot t_{inj in}),$$

$$(7)$$

where  $\dot{m}_g$  is the mass flow rate of the flue gases, kg/s,  $c_{p g out, in}$  is the specific heat of flue gases at the outlet and inlet temperatures, respectively kJ/kg °C,  $t_{g in, out}$  is the inlet and outlet temperatures of flue gases, respectively, °C, r is the latent heat of condensation, kJ/kg,  $c_{p inj out, in}$  is the specific heat of injected water at the outlet and inlet temperatures, respectively kJ/kg °C,  $t_{inj in, out}$  is the inlet and outlet temperatures of injected water at the outlet and inlet temperatures, respectively kJ/kg °C,  $t_{inj in, out}$  is the inlet and outlet temperatures of injected water, respectively, °C. Other parameters are the same as in equations above.

The total heat quantity (kW) recovered from flue gases:

$$Q_t = \dot{m}_g (c_{pg_{in}} \cdot t_{g in} - c_{pg_{out}} \cdot t_{g out}) + r \cdot \dot{m}_c, \tag{8}$$

where all parameters are the same as in equation 7.

The error (disbalance) of the above mentioned heat quantities was calculated as:

$$\operatorname{Error} = \frac{(Q_b - Q_w)}{Q_b} \times 100\%$$
(9)

The dew point temperature at the inlet to the calorimetric tube was calculated based on inlet relative humidity  $(RH_{in})$  and  $t_{in}$  and using equations presented in [11].

#### **RESULTS AND THEIR ANALYSES**

The experimental investigations were performed for turbulent flow (Re  $\approx$  18500) regimes. Initially, experiments were conducted without water in the calorimetric tube, and later water of 20 °C degrees was injected into the calorimetric tube. The mass fraction of water vapour in flue gases at the inlet (before the injection of water) was about 17–19 %.

Fig. 2 presents a typical distribution of temperatures along the test section (the model of the condensing heat exchanger) without and with water injection. It is known that when the

wall temperature is lower than the dew point temperature, water vapour starts to condensate on the wall. When the temperature of flue gases in the centre of the calorimetric tube reaches the dew point temperature, water vapour should start to condense in all its volume.



Fig. 2. Temperature distribution along the model of the condensing heat exchanger without (a) and with water injection (b): 1 marks the centre of the calorimetric tube, 2 marks the inner wall of the calorimetric tube, 3 marks cooling water in the space between the inner and the outer tubes, 4 marks the dew point temperature

In Fig. 2, the temperature variation of flue gases in the centre of the calorimetric tube is different compared to the temperature variations of the tube wall and cooling water. The flue gases temperature in the centre of the calorimetric tube almost linearly decreases to  $x/d \approx 110$  until the flue gases temperature at the wall of the calorimetric tube reaches the dew point temperature. Thus, till  $x/d \approx 110$ , the heat is transferred by convection. From  $x/d \approx 110$  to  $x/d \approx 170$ , when the flue gases temperature in the centre of the calorimetric tube reaches the dew point temperature, a change in the flue gases temperature character can be observed: it fluctuates but remains practically constant. In a previous study [12], it was observed that temperature fluctuations were noticeable usually when the flue gases temperature dropped below the dew point temperature. Small flue gases temperature fluctuations in this section of the calorimetric tube indicate that water vapour condenses intensively, likely in the all volume. The heat transfer by specific and latent heat is also confirmed by the temperature distribution

of cooling water. The cooling water temperature distribution character can also be divided into a few zones, which correspond to the above-mentioned flue gases temperature variation zones. The cooling water temperature and the tube wall temperature increase from the cooling water inlet at x/d=170 till  $x/d \sim 130$  can be noticed. An increase in the cooling water temperature from 40 °C (from inlet) to 65 °C, when the flue gases temperature in the centre is almost constant, indicates a high intensity of latent heat transfer. From  $x/d \sim 130$  till x/d = 0 the cooling water temperature increases by only about 10 °C degrees (from 65 °C to 75 °C). The change in the water temperature character from the parabolic to the linear coincides with the condensation process in the range from  $x/d \approx 110$  to  $x/d \approx 130$ . In the range where heat was transferred only by convection, the smallest increase in water temperature was obtained.

When water was injected into the calorimetric tube (Fig. 2 b), the character of the flue gases temperature distribution in the centre of the calorimetric tube became much more complicated. The injected water not only formed a film between the flue gases and the tube wall but also participated in the heat and mass transfer processes. The temperature of flue gases at the inlet was about 116 °C degrees, but along the distance from the beginning till  $x/d \approx 15$ , the temperature of the flue gases in the centre of the calorimetric tube showed a drastic decrease. This decrease may indicate that injected water not only cools down the tube wall, but also has some effect on the thermocouples installed in the centre of the tube.

In the range from  $x/d \approx 20$  to  $x/d \approx 80$ , a fluctuating decrease in the flue gases temperature was determined. The wall temperature was below the dew point temperature and a decrease of the flue gases temperature in the centre of the calorimetric tube showed that the condensation process was going on and the heat from flue gases was transferred to the film by convection and condensation. A temperature fluctuation could also show fog formation in the cross-section of the calorimetric tube. The flue gases temperature from  $x/d \approx 80$  to the end of the calorimetric tube was almost constant and close to the dew point temperature. This indicated that the condensation intensity increased and water vapour should start to condense in all its volume.

From Fig. 2 we can see that the temperature of the injected water at the inlet was lower than the temperature of the cooling water, and it cooled down the wall temperature and even slightly the cooling water temperature.

Table 1 and Fig. 3 present the comparison of heat balance between flue gases and cooling water with and without water injection into the calorimetric tube.

No.	Heat quantity	Without water	With water	
		injection, kW	injection, kW	
1.	Heat removed by cooling water, $Q_w$	1.91	1.45	
2.	Total heat recovered from flue gases, $Q_t$	1.98	2.48	
3.	Heat used for the heating of injected water	0	1.08	
4.	Heat quantity from flue gases excluding the	1.98	1.40	
	quantity used for the heating of injected water,			
	$Q_{h}$			

Table 1. Heat quantities

As we can see from the table above, the total heat removed from the flue gases is higher in the case of water injection; however, a rather big quantity is used for the heating of the injected water. There is a difference between the heat recovered from flue gases and removed by cooling water, and this is related to the heat loses through the test section walls. These errors are about 3–4 %. Thus, in general the heat balance is rather good (Fig. 3).



Fig. 3. Heat balance between flue gases and cooling water: 1) without water injection into the calorimetric tube; 2) with water injection into the calorimetric tube

# CONCLUSIONS

After performing temperature distribution measurements along the model of the condensing heat exchanger without and with water injection into the calorimetric tube, the following conclusions can be made:

- The injection of water has a significant impact on water vapour condensation from flue gases.
- The total heat removed from flue gases is higher (0.5 kW) in the case of water injection; however, a rather big quantity (1.08 kW) is used for the heating of the injected water.
- When no water was injected into the tube, convection prevailed in the initial part of the tube. However, with water injection condensation prevailed from the beginning of the tube.

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# AERODYNAMIC CHARACTERISTICS OF NACA 0015 AIRFOIL HAVING DIFFERENT ASPECT RATIO WITH END PLATES

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#### ABSTRACT

An experimental study is carried out to investigate aerodynamic characteristics of NACA 0015 airfoil having different aspect ratio with the endplates. The aspect ratio (AR) is varied between 1 and 4 with an increment of 1. AR of the airfoil is the ratio of spanwise length to mean chord. Lift and drag forces are measured with the help of a six-axis load cell on the flow around NACA 0015 airfoil at Re=  $7 \times 10^4$  and  $1.1 \times 10^5$ . This airfoil has a chord of 115 mm and a spanwise of 115 mm, 230 mm, 345 mm, and 460 mm. Force measurement results reveal that lift curves are significantly varied with increasing aspect ratio. Optimum L/D, indicating the aerodynamic performance of the airfoil, is obtained with aspect ratio of 4 at Re=  $7 \times 10^4$  and  $1.1 \times 10^5$ . Stall angles for AR4, AR3, AR2, and AR1 are  $\alpha = 10^\circ$ ,  $11^\circ$ ,  $12^\circ$ , and  $26^\circ$ , respectively. Results indicates that the lift coefficient performance enhances with increasing aspect ratios from 1 to 4 and stall angle significantly postpone with decreasing aspect ratios from 4 to 1.

Keywords: NACA 0015 Airfoil, Stall, lift coefficient, the drag coefficient

#### **INTRODUCTION**

Recent studies about UAV (Unmanned aerial vehicle) and MAV (Micro air vehicle) aerodynamics in low-to-mid Reynolds number has aroused interest during the last several decades. In the low-to-mid Reynolds number regime, airfoils present different aerodynamic characteristics, which are related to lift coefficient curve, maximum lift force, shifting stall angle, minimum drag force, post-stall and pre-stall curves of the drag coefficient. In low Reynolds regime (Re<10<sup>5</sup>), laminar boundary separation, transitional separation bubble [1], wing tip vortex [2], and vortex structures in the wake region of the airfoils [3] has a critical role for the airfoil aerodynamics as well as the airfoil cross-sections of aerodynamic features that are related to varied aspect ratio of the wing or airfoil. The airfoil surface area and geometrical features can be changed to increase lift force and to decrease drag force; furthermore, the drag and lift forces of an airfoil is directly connected with fluid-structure-interaction between the airfoil structure and the flow around the airfoil. Therefore, designing and optimization of the airfoil structure considering the aspect ratio acts a significant role in the airfoil aerodynamics.

In literature, researchers focus deeply on the performance of the larger aircraft; however, there is a need for research of the smaller aircrafts [4]. Moreover, it is reported that airfoil with low aspect ratios ( $2\ge$ AR) show different aerodynamic properties, so a more detailed aerodynamic analysis will be useful to Reynolds number of  $3\times10^6$  and  $6\times10^6$  and aspect ratio [5]. In the experimental study of Gabriel and Mueller [6], it is reported that the aerodynamic performance of various planforms is different from that of low-aspect-ratio wings in high Reynolds number. Also, they mentioned that the aspect ratio is a very important parameter for the aerodynamic characteristics of an airfoil. Taira and Colonius [7] mentioned that wings at post-stall angles of attack, unsteady separated flow and vortex dynamics behind low-aspectratio wings are not studied in details. Awasthi et al. [4] studied a wall-mounted NACA 0012 airfoil having symmetric and maximum thickness of  $0.12\times c$  for an aspect ratio of 0.5 in Reynolds number of 274,000. They reported that there is an important relation between tip, airfoil and junction flow that give rise to a 3D flow field across the span of a low aspect ratio

airfoil. Mizoquchi and Itoh [8] studied a flat plate with an aspect ratio smaller than 1 and they reported that the maximum lift coefficient and the stall angle are improved significantly. Sharma and Poddar [9] investigated the NACA0015 airfoil aerodynamic properties for aspect ratio of 1 at Reynolds number between 200,000 and 600,000. They concluded that the laminar separation bubble changed its position towards upstream by increasing AoA when separation near the leading edge gives rise to stall. Francis and Kennedy [10] used NACA 64009 airfoil for the investigation of the aspect ratio of 1.5 at Reynolds number of 247,000. They mentioned that tip vortex roll-up starts upside of five percent of chord location. In addition, the vorticity inboard of the tip is not related to AoA, but it is a function of aspect ratio. Pröbsting and Yarusevych [11] studied NACA 0012 with an aspect ratio of 2 at Reynolds number between 65,000 and 450,000. They found that the separation bubble is observed and the shear layer vortices over the trailing edge led to narrow the shedding frequency band. Yarusevych et al. [12] examined a NACA 0025 airfoil at a range of airfoil chord Reynolds numbers 55,000 -210,000 with an aspect ratio of 3. They showed that coherent vortices, which are broken down occurs during laminar separation, but these vortices can interact with the wake of the airfoil. Huang and Lin [13] investigated NACA 0012 airfoil that has 5 aspect ratio at a lower than Reynolds number of 20,000. They reported that the boundary layer does not reattach in the junction region and reattachment in the tip region is delayed in presence of suction-side separation.

The effects of the aspect ratio are unclear in the literature for low Reynolds number. Therefore, The aim of the paper is to clarify the effects of aspect ratio (AR) changing between 1 and 4 at such a low Reynolds number  $(7 \times 10^4 \text{ and } 1.1 \times 10^5)$  by performing the force measurement. Lift and drag forces are measured with the help of 3 axis load cell on the flow around NACA 0015 airfoil at Re=  $7 \times 10^4$  and  $1.1 \times 10^5$ .

#### **EXPERIMENTAL SETUP**

Aerodynamic measurements were carried out in an open type wind tunnel located at Mechanical Engineering Department, Karadeniz Technical University, Turkey. Dimensions of the test chamber are 570 mm x 570 mm x 1200 mm. Turbulence intensity is below 1% in the test chamber. Reynolds numbers based on the chord are  $7 \times 10^4$  and  $1.1 \times 10^5$ . A schematic view of the force measurement setup is given in Fig. 1. This setup is composed of a NACA 0015 model, end plates, a load cell, rotary unite, connection rod and ring. As presented in Fig. 1, NACA 0015 airfoil models were vertically placed to a six-axis load cell and there are two endplates on the top and bottom side of the airfoil to provide uniform flow acting on the model. The endplate at the top is movable in order to adjust according to changing spanwise of the airfoil models. Rotary unite helps to adjust the angle of attack changing between 0° and 30° an increment of 1 degree. The ring is used to protect the connection rod from acting undesired forces. Aerodynamic forces such as lift and drag were measured by using ATI GAMMA SI-32-2.5 model six-axis load cell. Six-axis of the load cell include  $F_x$ ,  $F_y$ ,  $F_z$ ,  $M_x$ ,  $M_y$ , and  $M_z$ . 20,000 force data were collected during 20 second with the help of NI PCIe-6323 DAQ card.



Fig. 1. Schematic view of the force measurement setup

NACA 0015 airfoil section was chosen because it can be utilized wind turbine blade and micro air vehicles (MAV). A schematic view of the airfoil models is shown in Fig. 2. Four airfoil models having different spanwise length were design. These models were manufactured from PLA material through a 3D printer. The estimated uncertainty for drag and lift coefficients is 3.2% and 2.6%. The estimated uncertainty for the angle of attack is  $\pm 0.2\%$ .



Fig. 2. Schematic view of the NACA 0015 airfoil with different aspect ratios

These models have a chord (c) of 115 mm and spans (s) of 115 mm, 230 mm, 345 mm, and 460 mm. Aspect ratio (AR) of the airfoil is the ratio of spanwise length to mean chord. Aspect ratios (ARs) are varied between 1 and 4 with an increment of 1. These models with ARs of 1, 2, 3, and 4 were denoted as AR1, AR2, AR3, and AR4, respectively.

#### **RESULT AND DISCUSSION**

The effect of the aspect ratio for NACA 0015 airfoil on the aerodynamic characteristics was investigated at  $\text{Re} = 7 \times 10^4$  and  $1.1 \times 10^5$ . In Fig. 3 the variation of lift coefficient as a function of angle of attack for AR = 1, 2, 3, and 4 at Re =  $7 \times 10^4$  is indicated. The lift coefficient (C<sub>L</sub>) of NACA 0015 airfoil with AR=4 shows a reasonably similar trend with airfoil theory represented by  $2\pi\alpha$  up to the angle of attack of 6° but the other models present a lower trend than the airfoil theory line. While the aspect ratio decreases from 4 to 1, the stall angle significantly postpone. While the aspect ratio decreases, stall characteristic of the airfoil models markedly change. Stall angles for AR4, AR3, AR2, and AR1 are  $\alpha = 10^\circ$ , 11°, 12°, and 26°, respectively.



Fig. 3. Lift coefficient variation of NACA 0015 airfoil with the aspect ratios of 1, 2, 3, and 4 at  $Re=7\times10^4$ .

The drag coefficient (C<sub>D</sub>) variations of AR1, AR2, AR3, and AR4 models are given in Fig. 4 for the Reynolds number at Re =  $7 \times 10^4$ . AR4 and AR3 showed a lower drag coefficient than AR1 and AR2 up to  $\alpha = 11^\circ$ . After this angle, there is a marked increase in the drag coefficient for AR4 and AR3 because of the stall situation. Thin airfoil theory ( $2\pi\alpha$ ) assumes that airfoil span reaches to infinity. That is to say, the airfoil has an infinity aspect ratio. The slope of the lift coefficients for AR1, AR2, AR3, and AR4 models is close to the airfoil theory line with an increasing aspect ratio.



Fig. 4. Drag coefficient variation of NACA 0015 airfoil with the aspect ratios of 1, 2, 3, and 4 at  $Re=7\times10^4$ .

Fig. 5 shows the variation of  $C_L$  for AR1, AR2, AR3, and AR4 as a function of angles of attack at Re= $1.1 \times 10^5$ . As it was in Re= $7 \times 10^4$  case, there is a strong relationship between overall lift performance and stall angle at Re =  $1.1 \times 10^5$ . When the aspect ratio decreases from 4 to 1, the stall angle postpone from 10° for AR4 to 26° for AR1. On the other hand, overall lift performance enhances with an increasing aspect ratio from 1 to 4.



Fig. 5. Lift coefficient variation of NACA 0015 airfoil with the aspect ratios of 1, 2, 3, and 4 at  $\text{Re} = 1.1 \times 10^5$ .

Drag coefficient results are given in Fig. 6 for the comparison of NACA 0015 airfoil with AR = 1, 2, 3, and 4 at Re =  $1.1 \times 10^5$ . The drag coefficients of AR3 and AR4 are similar at the pre-stall region that are lower angles of attack of 11 degrees. The same trend can be observed in the case of AR1 and AR2. The drag coefficient variations of AR3 and AR4 are lower than those of AR1 and AR2 at the angle of attack ranges 0°- 11° and 20° - 30°.



Fig. 6. Drag coefficient variation of NACA 0015 airfoil with the aspect ratios of 1, 2, 3, and 4 at  $\text{Re} = 1.1 \times 10^5$ .

Fig. 7 (a) and (b) show the lift to drag ratios (L/D) as a function of the angle of attack for AR1, AR2, AR3, and AR4 models at  $\text{Re} = 7 \times 10^4$  and  $1.1 \times 10^5$ , respectively. L/D ratios for all models show a similar trend after AOA= 20° indicating post-stall region at  $\text{Re} = 7 \times 10^4$  and  $1.1 \times 10^5$ . In terms of the overall performances of the airfoil, the optimum aspect ratio is 4 for all Reynolds number. Moreover, overall performances of the airfoil reduce with decreasing aspect ratios from 4 to 1 because the airfoils having high aspect ratios has lower drag and higher lift.



Fig. 7. Lift to drag ratio of NACA 0015 airfoil with the aspect ratios of 1, 2, 3, and 4 at (a)  $Re=7\times10^4$  and (b)  $1.1\times10^5$ 

## CONCLUSION

Aerodynamic characteristics of the NACA 0015 airfoil model with different aspect ratios were experimentally investigated in the suction type wind tunnel at  $Re=7\times10^4$  and  $1.1\times10^5$ . Forces acting on NACA 0015 airfoil is measured via a six-axis load cell. Force measurement results indicated that there is a strong relationship between lift curve and aspect ratios for all Reynolds number. When aspect ratios decrease from 4 to 1, stall angle significantly postpone. Overall lift performance enhances with an increasing aspect ratio from 1 to 4. L/D of NACA 0015 airfoil improves with an increasing aspect ratio from 1 to 4 for all Reynolds number.

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# AERODYNAMIC PERFORMANCE OF LEADING-EDGE TUBERCLE OF TAPERED SWEPT-BACK NACA 0020 AIRFOIL

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#### ABSTRACT

An experimental investigation has been conducted to determine the effects of leading-edge tubercles of tapered swept-back NACA 0020 airfoil at a suction type of wind tunnel. Force measurement experiment is carried out with the help of a six-axis load cell for the Reynolds number of  $1.0 \times 10^5$  at the angle of attack range of  $0^\circ - 30^\circ$  at an increment of one degree. NACA 0020 airfoil dimensions with and without leading-edge tubercle are a mean chord (c) of 89 mm and a spanwise length of 270 mm. Amplitude and wavelength parameters of the tubercle models are  $a_1 = 0.005c$ ,  $\lambda_1 = 0.25c$  for the first model and  $a_2 = 0.005c$ ,  $\lambda_2 = 0.5c$  for the second model. All models having a 30° sweep angle and taper ratio of 0.4 was fabricated with the help of a 3D printer from PLA material. For angles of attack between  $8^\circ \le \alpha \le 30^\circ$ , the B1 wing, having a smaller wavelength generated the highest lift. Also, B1 wing generated the lowest drag for angles of attack between  $7^\circ \le \alpha \le 20^\circ$ . Force measurements reveal that the tapered sweptback NACA 0020 airfoil models with the leading-edge tubercles showed better lift and drag performance when compared to baseline airfoil at the pre-and post-stall regions. The leading-edge tubercles markedly delay stall and help to suppress the undesired fluctuating forces that occurred in the case of the stall situation as compared to the baseline model.

Keywords: NACA 0020 airfoil, lift coefficient, drag coefficient, swept-back, leading-edge tubercles

#### **INTRODUCTION**

The humpback whale has rounded tubercles interspersed along its leading edge. Earlier studies on the application of leading-edge tubercles focus on the use of this geometric structure as a passive control device. Fish and Battle suggested that the flippers' tubercle structure can be used for flow control [1]. The maneuverability of the humpback whale has been attributed to its feeding behavior.

Miklosovic et al. examined the aerodynamic effects of leading-edge tubercles on humpback whale flippers [2]. They used idealized flipper models one with and one without leading-edge tubercles. Experiments carried out in wind tunnel with the Reynolds number in the range of  $5.05 \times 10^5 - 5.20 \times 10^5$  and the angles of attack between  $-2^\circ - 20^\circ$  and the results showed that the leading-edge tubercles delay the stall angle. In addition to delaying the stall angle up to 40 %, increased lift by 6 %, decreased the drag by 32 %.

Johari et al. measured the aerodynamic forces and examined the effects of leading-edge tubercles on the NACA 63<sub>4</sub>-021 airfoil at Re =  $1.83 \times 10^5$  in a water tunnel [3]. They used 3 different amplitudes (0.025c, 0.05c and 0.12c) and 2 different wavelengths (0.25c and 0.50c) values for considered models. They observed an increase in lift coefficient in the post-stall region. Results showed that the wavelength of the wing had a slight effect while the amplitude had a significant effect on the resulting forces and moments. They also performed the tuft flow visualization method to understand the flow characteristics and showed that flow separation occurred between the adjacent troughs of tubercles. Hansen et al. investigated the effects of leading-edge tubercles on different airfoil profiles with different aerodynamic characteristics at Re =  $1.2 \times 10^5$  [4]. According to the results, reducing the wavelength improve the post-stall characteristic. Also, they suggested that tubercles act in a similar way as vortex generators.

Custodio et al. investigated the effect of sinusoidal leading-edge on the aerodynamic characteristics of the NACA 634-021 airfoil at Reynolds numbers up to  $4.5 \times 10^5$  and angles of attack up to  $30^{\circ}$  [5]. They used full span, finite span, swept leading edge, and flipper models. Results showed that an exception of flipper models, all the modified models generated higher drag and had less lift to drag ratio compared to the baseline models.

Wei et al. experimentally investigated the hydrodynamic characteristics of the NACA 63<sub>4</sub>-021 airfoil with the leading-edge tubercle in the water tunnel at  $\text{Re} = 1.4 \times 10^4$  [6]. They revealed that the presence of tubercles improved flow separation characteristics and the larger amplitude and smaller wavelengths performed better. Also, they confirmed that the tubercles behave in a similar way as vortex generators. Another related research about tapered swept wings was carried out to investigate the flow separation characteristics by Wei et al. [7]

Abrantes et al. investigated pairs of models that each pair is comprised of a normal and tubercled configuration to understand the effects of parameters like taper ratio and sweep angle at  $\text{Re} = 8 \times 10^4$  and  $\text{Re} = 2 \times 10^5$ . They proposed that the optimum wing planform configuration for aircraft design at low Reynolds number could be the wavy swept wing. [8] Bolzon et al. investigated the effects of the tubercles on swept-tapered wing for low angles of attack at  $\text{Re} = 2 \times 10^5$ . [9] The NACA 0021 wing had swept angle of 35° and taper ratio of 0.4. Results showed that the presence of tubercles resulted in a reduction in lift for all angles of attack considered.

In this paper, swept wing geometry which is used from unmanned air vehicles to passenger aircraft was chosen. The purpose of this experimental study, investigate the effects of leading-edge tubercles on tapered swept-back NACA 0020 airfoil having different wavelength by considering the geometry of the humpback whale flipper.

#### METHODOLOGY

The experiments were carried out in an open circuit wind tunnel in the Mechanical Engineering Department of Karadeniz Technical University. The wind tunnel had a working section of 570 mm wide, 570 mm high and 1200 mm long. The turbulence intensity of the wind tunnel was smaller than 1 %. Freestream velocity in the test section was adjusted with a frequency inverter.

A schematic diagram of the wind tunnel test-section is given in Fig. 1. The experimental setup consists of an endplate, connection rod, protection pipe, test model, load cell and rotary unite. The wings were fixed vertically, and they placed in the test section by adjusting the gap between the endplate and the wings to be 1 - 2 mm. Force measurements were implemented with a 6-axis ATI Gamma DAQ F/T load cell. Force data were collected as 20000 data at a sampling frequency of 1000 Hz.



Fig. 1. Schematic of the experimental set-up

In this study, one baseline and two modified wings were used and their geometric details are shown in Fig. 2. One baseline and two modified tapered swept-back wings were investigated at  $\text{Re} = 1.0 \times 10^5$  (based on the mean chord length) for the angles of attack between  $0 - 30^\circ$ . The three wings having NACA 0020 airfoil profile were manufactured by using a 3D printer from PLA material. All wings have a mean aerodynamic chord c = 89 mm and span s = 270mm. The dimensions were chosen to minimize blockage effects and the blockage ratio was less than 6 %.

All wings have a root chord of 120 mm, a tip chord of 48 mm, and a taper ratio of 0.4. The sweep angle is  $\Lambda = 30^{\circ}$ . The modified wings were created by using cosine or sinusoidal function. In Equation (1), the amplitude (a) refers to the half distance between a tubercle peak and trough, and the wavelength ( $\lambda$ ) refers to the distance from trough to trough or from peak to peak. The tubercle configuration corresponds to Johari et al. [4]. B1 has an amplitude of a = 0.05c and a wavelength of  $\lambda = 0.25c$ . B2 has an amplitude of a = 0.05c and a wavelength of  $\lambda = 0.25c$ . B2 has an amplitude of a = 0.05c and a wavelength of  $\lambda = 0.25c$ . B2 has an amplitude of a = 0.05c and a wavelength of  $\lambda = 0.25c$ . B2 has an amplitude of a = 0.05c and a wavelength of  $\lambda = 0.25c$ . B2 has an amplitude of a = 0.05c and a wavelength of  $\lambda = 0.25c$ . B2 has an amplitude of a = 0.05c and a wavelength of  $\lambda = 0.25c$ . B2 has an amplitude of a = 0.05c and a wavelength of  $\lambda = 0.25c$ . B2 has an amplitude of a = 0.05c and a wavelength of  $\lambda = 0.25c$ . B2 has an amplitude of a = 0.05c and a wavelength of  $\lambda = 0.25c$ . B2 has an amplitude of a = 0.05c and a wavelength of  $\lambda = 0.5c$ . The amplitude and wavelength values were given in Table 1.

$$F(x) = (a^{*}\cos((2^{*}\pi^{*}x)/\lambda)).$$
(1)



Fig. 2. Schematic of the experimental set-up

Table 1. Wavelength and amplitude values of wings

Model	Amplitude (a)	Wavelength (λ)
B1	0.05c(4.45mm)	0.25c(22.25mm)
B2	0.05c(4.45mm)	0.5c(44.5mm)

Uncertainty analysis was applied as outlined by Coleman and Steele [10]. The estimated uncertainty for drag and lift coefficients is 3.2% and 2.6%. The estimated uncertainty for the angle of attack is  $\pm 0.2\%$ .

# **RESULTS AND DISCUSSIONS**

The parameters describing the aerodynamic forces, the lift and drag coefficients were determined using  $C_L=2L/\rho V^2 A$  and  $C_D=2D/\rho V^2 A$ , where L and D are the lift and drag forces, respectively,  $\rho$  is the air density, V is the freestream velocity, and A is the planform area for the wing. Graphical values were plotted versus the angle of attack by calculating the lift and drag coefficients of the wings. The lift coefficients for baseline and modified wings are presented in Fig. 3. The baseline, B1, B2 wings have approximately similar characteristics for angles of attack below 8°, while lift coefficient is lower for modified wings than the baseline at angles of attack considered.

For the baseline model, the lift coefficient decreases suddenly where stall occurring at 23°. For baseline wing reaching maximum values of lift coefficient approximately at  $\alpha = 23^{\circ}$ . The lift coefficient of the modified wings (B1 and B2) was greater than that of the baseline wing angles of attack in the range of  $8^{\circ} \le \alpha \le 30^{\circ}$ . Lift coefficient variation of B1 and B2 wings showed better performance than that of the baseline wing after  $\alpha = 8^{\circ}$ . B1 and B2 have softened the stall and increased the lift coefficient. For B2 wing reached a maximum value of lift coefficient (0.8247) at  $\alpha = 22^{\circ}$ . For B1 wing reached a maximum value of lift coefficient (0.7907) at  $\alpha=26^{\circ}$ . At the angle of attack 26°, the maximum lift coefficient of B1 was higher approximately by 10 % compared to the baseline wing. At the angle of attack 22° the maximum lift coefficient of B2 was higher approximately by 15 % compared to the baseline wing. It appears that the wing with shorter wavelength protuberances generated more lift than the longer wavelength wing at angles of attack range of  $8^{\circ} \le \alpha \le 30^{\circ}$ . This result was supported by the results of Johari et al. [3]. For the baseline wing, the trend of the lift coefficient was also similar to the results of Abrantes et al. [7].





Fig. 4 shows the comparison of the drag coefficients for the baseline and B1, B2 modified models at Re =  $1.0 \times 10^5$ . Until the angle of attack  $\alpha = 24^\circ$ , modified wings generate less drag compared to baseline wing. An exception of angles of attack between  $24^\circ - 30^\circ$ , the drag coefficient of the baseline wing is higher than those of B1 and B2 modified wings in all attack angles. After  $\alpha = 24^\circ$ , there is a similar trend in drag coefficient for Baseline, B1 and B2 wings.

Similar to the lift coefficient trend, B1 wing having a shorter wavelength generated less drag than the B2 wing having a longer wavelength wing before  $\alpha = 24^{\circ}$ . It is seen that the wing with shorter wavelength generate less drag than the longer wavelength wing over the majority of angles of attack examined. The present study is consistent with the observations of Johari et al. [3]



Fig. 4. Comparison drag coefficients for baseline and B1, B2 wings at  $Re = 1.0 \times 10^5$ 

A comparison of the lift to drag (L/D) ratio for baseline and modified wings are shown in Fig. 5. It is observed that the aerodynamic performance of the modified wings has a higher L/D than that of the baseline wing for all the angles of attack considered. Also, it is seen that the modified wing B1, provides the highest L/D ratio with its highest lift and lowest drag compared to baseline and B2 wings.



Fig. 5. Comparison Lift/Drag ratio for baseline and B1, B2 wings at  $Re = 1.0 \times 10^5$ 

Fluctuating lift force was defined as Equation (2) where  $F_i$  is instantaneous fluctuating lift force,  $\overline{F}_L$  is average lift force and *n* is the number of samples.

$$F_L' = \sqrt{\frac{1}{n} \sum_{i=1}^n \left(F_i - \overline{F}_L\right)^2} \,. \tag{2}$$

The fluctuating lift coefficient (C<sub>L</sub>') was determined using  $C_L'=2\times F_L'/\rho V^2 A$ , where  $F_L'$  is fluctuating lift force,  $\rho$  is the density of air, V is the freestream velocity, and A is the planform area for the wing. A comparison of the fluctuating lift coefficient for baseline and modified wings are shown in Fig. 6. For the baseline wing, spikes indicate the flow characteristic has changed. For the baseline wing, stall occurred at 23° where the flow separation and strong vortex shedding causing a sudden drop in the lift coefficient. The slope of lift changed at the angle where the first spike occurred. The modified wings both generated higher lift and eliminated the spike value expressing the strong turbulence and flow instability occurring in the baseline wing.



Fig. 6. Comparison of fluctuating lift coefficient for Baseline, B1 and B2 wings at  $Re = 1.0 \times 10^5$ 

# CONCLUSION

The effect of the tubercle leading-edge for one baseline and two modified tapered sweptback wings were experimentally investigated at  $\text{Re} = 1.0 \times 10^5$  for the angles of attack between  $0^\circ - 30^\circ$  in an open-loop wind tunnel. Results revealed that the presence of leading-edge tubercles delay stall and resulted in an increment in the lift and a reduction of drag. For angles of attack between  $8^\circ \le \alpha \le 30^\circ$ , the B1 wing, having a shorter wavelength generated the highest lift. Also, B1 wing generated the lowest drag for angles of attack between  $7^\circ \le \alpha \le 20^\circ$ .

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# INVESTIGATION OF LEADING-EDGE TUBERCLE FOR TAPERED SWEPT-BACK AIRFOIL AT LOW REYNOLDS NUMBER

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#### ABSTRACT

The effects of leading-edge tubercles of tapered swept-back NACA 0020 airfoil were investigated experimentally at mean chord based Reynolds number of  $5.0 \times 10^4$  in an open circuit wind tunnel. Force measurement experiment performed with the help of six-axis load cell at the angle of attack range of  $0^{\circ}-30^{\circ}$  at an increment of one degree. NACA 0020 airfoil models having a mean chord of 89 mm and a spanwise of 270 mm are used in this study. The models consisted of three configurations, one model without leading-edge tubercles (baseline model) and two models with leading-edge tubercles. Tubercle geometry has amplitude of 0.075c and wavelengths of 0.025c and 1c. All models had 25° sweep angle and 0.4 taper ratio. In addition, all models' tip chord and root chord were 48 mm and 120 mm, respectively. The results showed that the leading-edge tubercles significantly enhance the aerodynamic performance of the models in terms of L/D at the pre-stall region and do not present the common stall characteristic as compared to the baseline model.

Keywords: NACA 0020 airfoil, stall, lift coefficient, drag coefficient, swept-back

# **INTRODUCTION**

Over the past years, biological organisms have been examined to improve engineering systems. The idea to investigate the effects of leading-edge tubercles on airfoil performance stems from humpback whale flippers. Fish and Battle suggested that the flippers' tubercle structure can be used for flow control by examining the morphological structure of the humpback whale flipper [1].

Miklosovic et al. investigated the aerodynamic effects of idealized flipper models one with and one without leading-edge tubercles at the Reynolds number between  $5.05 \times 10^5 - 5.20 \times 10^5$ , and results revealed that the presence of tubercles delays the stall angle [2]. Findings from this study showed that tubercle structure also improved stall characteristics. Johari et al. experimentally investigated the effects of leading-edge tubercles on the NACA  $63_4$ -021 airfoil performance at Re= $1.83 \times 10^5$  [3]. The amplitude and wavelength values were chosen ranged from 2.5 - 12% and 25 - 50% of the mean chord length, respectively, based on humpback whale morphology. They observed modified models generate as much as 50% more lift coefficient compared to the baseline model in the post-stall regime. They also found wavelength of tubercles had little effect on force coefficients. Hansen et al. compared NACA 0021 and NACA 65-021 airfoils to understand the influence of tubercle leading-edge at Re =  $1.2 \times 10^5$  [4]. They found that maximum lift coefficient occurred with the smallest tubercle amplitude for both airfoil profiles. The optimum configuration had an amplitude of 0.03c and a wavelength of 0.11c.

Custodio et al. used full span, finite span, swept leading edge, and flipper models and examined the effect of leading-edge protuberances on the aerodynamic characteristics of the NACA  $63_4$ -021 airfoil [5]. The lift and drag coefficients of swept leading-edge models were compared at Re=  $4.4 \times 10^5$ . The modified models generated an increase in lift compared to the baseline model at higher angles of attack. Also, they suggest that the swept-leading-edge airfoils may be the most practical planform geometry.

Many experimental and computational studies have been conducted to investigate the effect of leading tubercles. In these studies, mostly rectangular wings and whale flipper models were examined. However, few studies have examined the application of leading-edge tubercles on tapered swept-back wings. Wei et al. were investigated flow separation characteristics in a water tunnel [6]. The experiments were conducted at Reynolds numbers at Re=  $1.4 \times 10^4$  for two SD7032 tapered swept-back wings, one with a straight leading-edge and the other with tubercled wings. Results showed that the presence of leading-edge tubercles can alleviate flow separation downstream of both troughs and peaks. Wei et al. investigated aerodynamic characteristics and surface flow patterns for four tapered swept-back wings at Reynolds numbers from  $5.5 \times 10^4$  to  $4.2 \times 10^5$  [7]. Results showed that stall characteristics improved for modified wings when compared to the baseline wing. Flow visualization reveals that vortex structures of wings are similar.

Bolzon et al. investigated the effects of tubercles on tapered swept-back wings at low angles of attack at Re=  $2.2 \times 10^5$  [8]. Force measurements revealed that tubercles reduce lift and drag for angles of attack range of  $1^{\circ}$  -  $8^{\circ}$ . Furthermore, flow visualization showed that tubercles act like vortex generators.

The geometry of the humpback whale flipper has a unique leading-edge shape known as tubercles or wavy shape. By considering the geometry of the humpback whale flipper, the purpose of this experimental study is to examine the effects of leading-edge tubercles on tapered swept-back NACA 0020 airfoil having different amplitude at low Reynolds number.

## METHODOLOGY

The aerodynamic performance for three wings was investigated in an open circuit wind tunnel with the test section dimensions of 570mm × 570mm in the Mechanical Engineering Department of Karadeniz Technical University. Streamwise turbulence intensity of wind tunnel in test-section was smaller than 1%. The experimental setup shown in Fig. 1. consists of an endplate, connection rod, protection pipe, test model, load cell and rotary unit. Force measurements were carried out using a 6-axis ATI Gamma DAQ F/T load cell. The wings were fixed vertically and the gap between the endplate and wings were adjusted 1-2 mm. Measurements were taken for 20 s at a sampling frequency of 1000 Hz. Experiments were carried out at Re =  $5.0 \times 10^4$  an increment of 1 degree in the range of  $0^\circ \le \alpha \le 30^\circ$  of the angles of attack.



Fig. 1. Experimental set-up for the force measurement

Three tapered swept-back wings were produced using a 3D printer from PLA filament and sanded to obtain appropriate roughness. The three wings based on NACA 0020 airfoil profile and their geometric details are shown in Fig. 2.



Fig. 2. Geometric details of tapered swept-back wings

All wings have a mean chord of c=89 mm, the span of s=270 mm, planform area of A=0.023 m<sup>2</sup>, and sweep angle of  $\Lambda$  = 25 deg. Also, all wings have a root chord of 120 mm, a tip chord of 48 mm, hence producing a taper ratio of 0.4. The dimensions have been chosen to minimize the blockage effects. The blockage ratio was less than 6% for the maximum angle of attack.

$$F(x) = (a^* \cos((2^* \pi^* x) / \lambda)) \tag{1}$$

The modified A1 and A2 wings were created by implementing tubercles along the leading-edge using Equation (1). The amplitude (a) refers to the half distance between a tubercle peak and trough. The wavelength ( $\lambda$ ) refers to the distance from trough to trough or from peak to peak. A1 has an amplitude of a=0.025c and a wavelength of  $\lambda$ =1c. A2 has an amplitude of a=0.075c and a wavelength of  $\lambda$ =1c.

Uncertainty analysis is employed to use uncertainty method suggested by Coleman and Steele [9]. The uncertainty was accounted for by performing two runs for each wing. The estimated uncertainty for drag and lift coefficients is 3.2% and 2.6%. The estimated uncertainty for the angle of attack is  $\pm 0.2\%$ .

## **RESULTS AND DISCUSSIONS**

The lift and drag coefficients of the tapered swept-back wings measured and calculated for the Reynolds number of Re= $5.0 \times 10^4$ . Fig. 3. shows comparison of the lift coefficient for baseline and two modified models for the angle of attack between 0° and 30° with an increment of 1°. For the baseline model, stall occurring at 23° where the lift coefficient reaches the maximum value.



Fig. 3. Comparison of the lift coefficient for Baseline, A1, and A2 wings at Re= $5.0 \times 10^4$ .

The lift coefficient of the baseline model was greater than that of all modified models at the range of  $10^{\circ} \le \alpha \le 23^{\circ}$ . In all angles of attack, the A1 wing indicates a slightly higher lift coefficient than the A2 wing. The A2 wing generated minimum lift compared to the baseline and A1 wing. The lift coefficients of the A1 and A2 wings were greater than that of the baseline until 9° and 10°, respectively. The A1 wing generated less lift compared to the baseline at the range of  $10^{\circ} \le \alpha \le 23^{\circ}$ . After the angle of attack  $\alpha = 24^{\circ}$ , the A1 wing generated slightly more lift compared to the baseline wing.

Fig. 4. shows the comparison of the drag coefficients for the baseline, A1 and A2 modified wings at Re= $5.0 \times 10^4$ . At the range of angles of attack 19° - 30°, the drag coefficient of the baseline model is higher than those of A1 and A2 wings. The modified wings generate more drag as compared to the baseline wing at the range of  $8^\circ \le \alpha \le 14^\circ$ .

Fig. 4. shows the comparison of the drag coefficients for the baseline, A1 and A2 modified wings at Re= $5.0 \times 10^4$ . At the range of angles of attack 19° - 30°, the drag coefficient of the baseline model is higher than those of A1 and A2 wings. The modified wings generate more drag as compared to the baseline wing at the range of  $8^\circ \le \alpha \le 14^\circ$ .



Fig. 4. Comparison of the drag coefficient for Baseline, A1 and A2 wings at  $Re=5.0x10^4$ .

A comparison of the lift to drag (L/D) ratio for baseline and modified wings are shown in Fig. 5. It is observed that the aerodynamic performance of the modified wings has a higher L/D than that of the baseline wing for the angles of attack range of  $2^{\circ} - 9^{\circ}$ . It is seen that the modified wings A1 and A2 provided the less L/D ratio compared to baseline wing angles of attack  $8^{\circ} - 21^{\circ}$ .



Fig. 5. Comparison of the Lift/Drag for Baseline, A1 and A2 wings at  $Re=5.0 \times 10^4$ .

# CONCLUSION

In this study, the influence of the leading-edge tubercles on NACA 0020 tapered sweptback wings is experimentally investigated. Measurements carried out at Re=  $5.0 \times 10^4$  for the angles of attack between 0° - 30°. Results showed that even if the tubercle configuration does not improve the post-stall characteristics, they eliminate stall behavior. Modified models have almost the same increasing tendency before stall and L/D values of the modified wings showed better performance than the baseline wing at the angle of attack between 2° and 9°.

# ACKNOWLEDGEMENTS

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# AN EXPERIMENTAL STUDY ON FLOW AROUND NACA 0020 AIRFOIL WITH DIFFERENT SWEPT BACK ANGLE

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#### ABSTRACT

An experimental study is carried out to investigate the effects of the swept-back angle of the NACA 0020 airfoil at a suction type wind tunnel. The swept-back angle of the NACA 0020 airfoil was determined as 25°, 30° and 35°. These airfoil dimensions are a mean chord (c) of 89 mm and spanwise length of 270 mm. The tapered ratio of the airfoil, that is the ratio of its tip chord to its root chord length, is 0.4. The Reynolds number based on the mean chord is  $8x10^4$ . Force measurements experiment is performed by using the six-axis load cell at the angle of attack changing from 0° to 30° with an increment of one degree. The effect of the sweep-back angle is more pronounced for all models at  $\alpha > 7^\circ$ . The maximum lift coefficient was obtained with s25 model. According to force measurement results, the optimum swept-back angle was determined as 25 degrees. The results indicate that the swept-back angle enhances the lift characteristics and change the common stall characteristic.

Keywords: NACA 0020 Airfoil, swept-back, lift coefficient, drag coefficient

#### **INTRODUCTION**

Wing shapes for air vehicles have vital importance to provide lift, controllability, and manoeuvrability. Rectangular, delta, swept-back, tapered, etc. can be given as an example of the wing shapes. Swept-back and/or tapered wings have extensive application areas in the industry. The swept-back angle of the airfoil can decrease the drag and undesired effects at low Reynolds number [1]. These kinds of airfoils are significantly affected by the laminar separation bubble (LSB) formation that is closely related to its aerodynamic performance such as lift and drag [2].

Yen and Huang [3] investigated the effects of the swept-back angle between 0° and 45°, wide Reynolds number ranges, and angle of attack between 0° and 35° on the flow around the NACA 0012 airfoil model in terms of aerodynamic performance. Their results indicated that swept back airfoil postpone the stall angle for the different swept-back angles. According to these parameters, they also reported very different flow modes such as laminar separation, separation bubble, leading-edge bubble, the bubble burst, turbulent separation, bluff-body wake, three-dimensional flow, and turbulent boundary layer. In the other study of Yen and Huang [4], they examined flow and aerodynamic characteristics of swept-back NACA 0012 airfoil with a swept-back angle of 38°, Reynolds number of  $1.5 \times 10^4$ , and aspect ratio of 10. They performed smoke and oil flow visualization, force measurement, and PIV measurement. Their results indicated that, as in their previous work [3], different flow modes were also formed in the present study. They also found that aerodynamic characteristics of the swept-back wing are directly interested in changing surface flow patterns. Black [5] researched the flow pattern on a swept-back airfoil with a sweep angle of  $44^\circ$  with the help of pressure measurement, surface oil flow visualization, and tuft flow visualization method. The results indicated that the

swept-back wing leads to long and short LSB formation on the suction surface of the wing. Yen and Hsu [1] studied the wake and flow structure on the flow around the swept-back wing with a swept-back angle of 15°. They performed smoke wire flow visualization and particle image velocimetry (PIV) technique. They proposed five different flow modes, that are attached flow, instability wave in the wake, vortical wake, separation from near leading edge, and bluff-body wake, based on the angle of attack and Reynolds number. Hayostek and Amitay [6] performed an experimental study for the swept-back NACA 0015 airfoil having swept angles of 0°, 30°, and 45°, Reynolds number varied from 600 to 1200, and aspect ratios of 2, 4, and 6. They found that when swept angle increase, flow structure gradually become steady. It was also indicated that aspect ratios significantly affect vortex shedding characteristics. Gerontakos and Lee [7] investigated the flow pattern on the flow around the tapered swept-back NACA 0015 airfoil with the swept angle of 24° by using 7 hole pressure probe and force measurement system at  $Re=1.81 \times 10^5$ . Their results indicated the vortex pattern for swept-back tapered airfoil has similar behavior compared to the rectangular airfoil model. Biswas et al. [8] experimentally researched RAE 2822 airfoil with a swept back angle of 30° by using surface oil flow visualization. They observed a 3D vortex flow structure around the airfoil and laminar bubble separation formation. Papadopoulos [9] numerically investigated the effect of leading-edge tubercle on the flow around the NACA 0021 airfoil with a sweep angle of 33° at the Reynolds number ranges between  $5 \times 10^5$  and  $1 \times 10^6$ . Their results showed that tubercle produces a pair of counter-rotating vortices leading to stall delaying. Wei et al. [10] examined the aerodynamic performance of tapered swept-back SD7032 airfoil with leading-edge tubercles at the Reynolds number of  $5.5 \times 10^4$ . Their results revealed that the aerodynamic performance of the swept-back airfoil was enhanced with the help of leading-edge tubercles associated with surface and streamwise counter-rotating vortex pairs. In the other study of Wei et al. [11], they studied aerodynamics characteristics and flow patterns on the flow around the tapered swept back airfoil at Reynolds numbers. Tubercles are provided stall enhancement, lift increment and drag reduction.

This study aims to provide important insights about tapered swept-back airfoil at low Reynolds number and reveal the aerodynamic performance of tapered swept-back airfoil measure aerodynamic forces such as lift and drag on the flow around NACA 0020 having a different swept-back angle at  $Re=8\times10^4$ . This study is also desired to find the optimum swept-back angle in terms of lift and drag coefficient performance.

#### **EXPERIMENTAL SETUP**

Aerodynamic characteristics on the tapered swept-back wing were experimentally investigated at different swept angles and wide angles of attack ranges. Experiments were carried out at a suction type wind tunnel. The tunnel has  $57 \text{cm} \times 57 \text{cm}$  square test section with 120cm length. There are three screens packed to decrease the turbulence intensity in the test section. Turbulence intensity is lower than %1 for wide Reynolds number ranges. The free-stream velocity in the test section was measured with the help of a pitot-static tube. The force measurement experimental setup can be shown in Fig. 1. This setup consisted of the wind test section, a tapered swept-back airfoil, an endplate, six-axis load cell, a rotary unite, a connection rod, a ring of a connecting rod. The test model was mounted 45 mm over the test chamber floor. The airfoil model was placed 1 mm over the root of the tapered swept-back airfoil. This small gap between endplate and the test model is set due to both directly measure the forces and easily rotate the model without beating the endplate surface. On the tip side of the airfoil, there is no endplate. A rotary unite was used to precisely rotate the test models. The test models were rotated between 0° and 30° with an increment of 1° to measure the aerodynamic forces. The

connection rod connected the load cell and the test model to each other. The ring of the connecting rod was utilized to eliminate undesired forces acting on the airfoil. Aerodynamic forces such as lift and drag were measured by using ATI GAMMA six axis load cell. Force data were collected with the help of the NI PCIe-6323 DAQ card.



Fig. 1. Schematic view of the force measurement setup

The tapered swept-back airfoil was produced from PLA material with the help of 3D printer and this model is sanded from course to fine sandpaper to obtain a smooth surface. A schematic view of the airfoil models was given in Figure 2. The swept-back angle of the NACA 0020 airfoil was determined as  $25^{\circ}$ ,  $30^{\circ}$ , and  $35^{\circ}$ . These models with swept-back angles of  $25^{\circ}$ ,  $30^{\circ}$  and  $35^{\circ}$  were denoted as s25, s30, and s35, respectively. "s" also indicates the swept-back angle. These airfoil dimensions are a mean chord (c) of 89 mm and spanwise length of 270 mm. The tapered ratio of the airfoil, that is the ratio of its tip chord to its root chord length, is 0.4. The Reynolds number based on the mean chord is  $8x10^4$ .

Uncertainty analysis is employed to use the uncertainty method suggested by Coleman and Steele [10]. The estimated uncertainty for drag and lift coefficients is 3.2% and 2.6%. The estimated uncertainty for the angle of attack is  $\pm 0.2\%$ .



Fig. 2. Schematic view of the tapered swept-back airfoil at (a) 25°, (b) 30° and (c) 35°

#### **RESULT AND DISCUSSION**

Drag and lift force measurements were carried out to examine the effects of the swept-back angle with tapered on NACA 0020 airfoil at Re= $8x10^4$ . Variation of the lift coefficient for a tapered swept-back airfoil with the swept-back angle of  $25^\circ$ ,  $30^\circ$  and  $35^\circ$  were shown as a function of angles of attack (AOA) changing between in  $0^\circ$  and  $30^\circ$  Fig. 3. Up to  $\alpha = 7^\circ$ , there are no significant effects of swept-back angle over lift coefficient because all models showed similar variation. After this angle, the upward slope of the S30 and S35 models changed and continued increase with the lower slope without the stall. Moreover, the effect of the sweep angle is more pronounced for all models at  $\alpha > 7^\circ$ .



Fig. 3. Lift coefficient variation of tapered swept-back angle airfoil with 25°, 30°, and 35°.

While the stall angle of S30 and 35 is  $\alpha = 21^{\circ}$ , that of S25 is  $\alpha = 24^{\circ}$ . S25 model with the lowest sweep angle postponed the stall angle by 3 degrees when compared to S30 and S35 models. According to the lift plot, It was observed that both tapered and swept-back angles significantly change the deep stall characteristic observed in rectangular airfoil sections. This result was also supported by the results of Yen and Huang [3]. The variation of the drag coefficient for s25, s30, and s35 models as a function of angle of attack can be shown in Figure 4. S25 and S35 show similar trend up to AOA = 9°. After this angle, all models present a close variation to each other. The slope change observed in the lifting force results was not observed in drag coefficient results.



Fig. 4. Drag coefficient variation of tapered swept-back angle airfoil with 25°, 30°, and 35°.

Airfoil efficiency can be stated with lift to drag ratios (L/D). Figure 5 shows the L/D as a function of the angle of attack for s25, s30, and s35 models. After AOA= 9°, s25 and s30 have higher L/D ratios than the S35 model while L/D of S35 is greater than that of s25 and s30 before AOA= 9°.



Fig. 5. Lift to drag ratio variation of the tapered swept-back angle airfoil.

#### CONCLUSION

Aerodynamic characteristics of the tapered swept-back NACA 0020 airfoil model with sweep angles of 25°, 30°, and 35° were examined in the open type wind tunnel at Re=80000. Force measurement experiment is performed by using 6 axis load cell. The effect of the sweep-back angle is more pronounced for all models at  $\alpha > 7^\circ$ . The maximum lift coefficient was obtained with s25 model. According to force measurement results, the optimum swept-back angle was determined as 25 degrees. The results indicate that the swept-back angle enhances the lift characteristics and changes the common stall characteristic.

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# MOLECULAR DYNAMICS SIMULATION OF WATER FLOW INSIDE PLANAR NANOCHANNEL

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#### EXTENDED ABSTRACT

#### **OVERVIEW**

Nanofluidic devices are based on heat and mass transfer in nanochannels, and the development of such devices requires precise knowledge regarding fluid flows and fluid molecular interactions with the solids at the interphase. As the channel dimensions are reduced to a nanoscale, novel physical phenomena occur, which have promising applications in many fields of science, technology, and engineering. Such unique behaviour of fluids in nanoscale is related to the discrete nature of fluids' high surface-to-volume ratio, local density and temperature fluctuations and the variations of local viscosity inside the channel [1–3]. Furthermore, at the liquid-solid interphase, where the density of the fluid decreases from bulk density to zero, describing the flowing fluid is difficult due to layering effects near the walls, and the interpretation of flow boundary conditions becomes difficult because the conventional no-slip boundary condition cannot be applied [4]. Therefore, the fluid flows and flow parameters in nanoscale channels have been thoroughly studied both experimentally and numerically in recent years due to their novel physical behaviour and importance to many technological applications [1,5,6]. However, the experimental method still faces challenges related to nanoscale measurement; therefore, molecular dynamics (MD) simulations have become useful tools for studying fluid flows and mass transport properties in nanochannels and nanotubes [3,7–13].

#### **METHODS**

The MD simulation method was used to examine the effects of two different temperature control strategies in water flow inside planar nanochannel (Fig. 17). The water flow was induced by applying constant force in *x* direction on each water molecule. In first strategy, dynamics of copper wall atoms was not solved (fixed walls simulations) and the thermostat method was applied directly to water molecules. In second case, the dynamics of copper atoms was solved using embedded atom model (EAM) interatomic potential (dynamic walls simulations) and the thermostat was applied only to the copper atoms leaving water molecules to run in microcanonical ensemble. For water, SPC/E model was used to solve molecular interactions. The macroscopic parameters from the simulations were obtained by averaging molecular trajectories over time. MD simulations were performed using LAMMPS molecular dynamics code [14].



Fig. 17. Visual representation of simulated system. The periodic boundary conditions were applied in x, y and z axis

#### RESULTS

The peaks in number density profiles across the channel showed the layering effect of water molecules adjacent to the solid walls, which induced slip velocity as these molecules move in flow direction. Meanwhile, flow velocity in the bulk region of the channel was close to the parabolic profile. Finally, the induced slip velocity was linearly proportional to the flow inducing force.

#### CONCLUSIONS

In present paper, molecular dynamics simulations were used to study SPC/E water flows inside planar nanochannels and influence of temperature control strategies on flow behaviour. The following conclusions can be drawn from obtained results. The peaks in number density profiles of water showed water layering effect near the confining walls which was caused by corelated effects of molecular long-range attraction and short-range repulsion between copper and oxygen atoms. The flow velocity in the bulk region of the channel was close to the parabolic profile with velocity slip near the walls, which indicates disagreement with classical flow behaviour observed in macroscales. The mean velocity of water inside the channel and the velocity slip in near-wall region increase linearly with increasing the magnitude of the flow inducing force in simulations with both fixed and dynamic walls.

Keywords: Molecular dynamics; nanochannels; Poiseuille flow; velocity profile; slip velocity

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# EXPERIMENTAL AND NUMERICAL ANALYSIS OF THE FLOW STRUCTURE IN CAVITIES UNDER PULSATILE INLET FLOW CONDITIONS

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#### **OVERVIEW**

Flow over the backward-facing step is one of the most examined patterns for flow separation studies under stationary and pulsatile flow conditions. The situation becomes more complicated and not thoroughly investigated when the forward-facing step limiting the length of expanded channel length is present.

Forward-facing step significantly influences the structure of recirculation flow behind the backwardsfacing step. The effect of the pulsatile inlet flow conditions on the length of the recirculation zone depends on pulsation frequency and amplitude. It is known that pulsatile inlet flow conditions cause a reduction of the recirculation zone length. The strength of this effect directly depends on Womersley number (Wo) and may vary at different Reynolds number (Re) cases. Also, pulsatile inlet flow conditions strengthen the reverse flow; therefore, the fluid mixing in the cavity becomes more effective. In addition, pulsatile inlet flow conditions cause early appearance (Re wise) of the upper recirculation zone. In present work, transitional and closed-type cavities were investigated ( $L/h_1 = 10$ , 16) experimentally and numerically. Experimental measurements were performed to investigate the integral effects of pulsatile flow conditions on recirculation zone length, while CFD simulations revealed flow structure dynamics at different velocity angle phases.

#### **METHODS**

Commercially available computational fluid dynamics software *Ansys Fluent* was employed to perform numerical simulations in two different length-to-step height ratio cavities. For the experiments, the micro-particle image visualization method was used. Experiments were performed at  $Re_{Dh} = 200 - 2000$ 

and Wo = 0.28 – 0.55 in closed-type cavity, where  $Re_{Dh} = \frac{U \cdot D_h}{v}$  and  $Wo = \sqrt{\frac{\omega \cdot D_h}{v}}$ ; The numerical analysis was performed under different Wo and Re numbers as well (Re<sub>Dh</sub> = 200 – 2000; Wo = 0.28 – 0.62). In both numerical simulations and experimental measurements, the pulsation amplitude was set to a constant value of one. In order to compare numerical simulation results with experimental, the comparison under stationary flow conditions was made. The comparison showed that numerical simulation results are in good agreement with experimental results in the most of the investigated Re range.



Fig. 5 Scheme and dimensions of investigated cavities

Numerical simulations and experiments were performed in cavities with dimensions given in Fig. 1. Channel height-to-depth ratio of the transitional-type cavity was  $L/h_1 = 10$ , whereas for the closed-type cavity  $-L/h_1 = 16$ . Three recirculation regions can be observed from the scheme.  $x_C$ ,  $x_{UR}$ ,  $x_R$  are the lengths of corner eddy, upper recirculation zone, and primary recirculation zone, respectively. Channel expansion ratio ER = H/h = 2 was kept constant for all cases investigated.

For pulsatile flow the inlet velocity profile is assumed to be flat and can be described as a sinusoidal function:

 $U(\varphi) = U_0(A + \sin(\varphi));$ where U - velocity, m/s; A - amplitude;  $\varphi$  - pulsation phase angle, °.

#### RESULTS

Firstly, it is noted that the number of recirculation regions in the cavity depends on Re. In the case of Re = 400, two recirculation regions are observed (namely, primary recirculation zone and upper recirculation zone (Fig. 1)). As Re increases up to 2000, corner eddy between the backward-facing step and the primary recirculation zone appears.

Corner eddy was always absent at Re = 400 in both types of cavities. The presence of the upper recirculation zone in a closed-type cavity was observed only at certain velocity phase angles, as the velocity was increasing  $(270^{\circ} < \phi < 360^{\circ} \text{ and } 0^{\circ} < \phi < 90^{\circ})$  and decreasing  $(90^{\circ} < \phi < 270^{\circ})$  rapidly. The upper recirculation zone in both cavities at Re = 400 was absent at the  $195^{\circ} < \phi < 345^{\circ}$ . The results showed that all three recirculation zones lengths are affected by pulsatile flow frequency and Re number. It was noted that pulsatile inlet conditions at the same Re number values caused the reduction of the recirculation zone length. To analyze the development of the flow, the dependency of recirculation regions length on velocity phase angles was obtained. The geometry change had an impact on the flow structure as well. Cavity type impacts flow structure, as well as the influence of the forward-facing step, depends on the relative cavity length ( $L/h_1$ ). In a transitional-type cavity, the absence of flow reattachment is observed in the transitional flow regime. At the onset of the pulsation cycle, the velocity vectors show that the recirculation zone has the same size of steady flow at the same instantaneous Re. Experimental measurements revealed that time-averaged recirculation zone length decreases in the range of 15-28 % depending of pulsatile frequency compared to stationary flow.

#### CONCLUSIONS

The dynamics of recirculation regions in transitional and closed-type cavities were investigated under stationary and pulsatile flow conditions depending on Re and Wo numbers. Three distinct recirculation regions were identified – primary recirculation zone, upper recirculation zone, and corner eddy. The rapid growth of the primary recirculation zone was observed in the laminar flow regime in both types of cavities. As the flow regime started to transition to a turbulent flow regime, the main flow was lifted from the bottom of the channel. The absence of flow reattachment was observed when Re > 300 in a transitional-type cavity and when Re > 600 in a closed-type cavity, whereas the reattachment of the main flow became present at Re = 600 and Re = 1600, respectively. Experiments performed in a closed-type cavity under pulsatile conditions showed similar  $x_{\rm R}$  dependency on Re patterns. The present study revealed that the effect of primary recirculation zone length reduction occurred only in the transitional regime, after the flow reattachment on the bottom of the channel. The reduction effect varied from 15% to 28%.

**Keywords:** pulsatile flow, cavity, flow dynamics, flow structure, recirculation zone, computational fluid dynamics

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# ELECTRICAL PARAMETER MONITORING SYSTEM FOR SUPERCAPACITORS

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#### ABSTRACT

The research on supercapacitors has gained particular attention lately. The capacitance of supercapacitors (up to 2500 F/g) is up to a million times that of conventional capacitors. Supercapacitors operate on similar principles to conventional capacitors. However, their electrode surface area (up to  $2500 \text{ m}^2/\text{g}$ ) is significantly larger than conventional capacitors. The high-capacity supercapacitor is planned to be formed at the Lithuanian Energy Institute using plasma spray technology. After forming supercapacitors, it is very important to study their electrical performance (specific capacitance, operating voltage, stability of the double electric layer mechanism, influence of the number of charge-discharge cycles on efficiency, charge-discharge characteristic time, etc.). One of the parameters – charged - discharge. Stability is the object of the study. The classical capacitor charging/discharging method (semi-manual operation) is very time-consuming.

To solve this problem, a fully automated stand was designed and manufactured to analyse the performance characteristics of supercapacitors and collect scientific data. This charging unloading system is fully automated and remotely controlled.

The results of the measurements show that the charge-discharge peaks have good repeatability during the operation of the supercapacitors; thus, the number of charge-discharge cycles does not influence the structure of the carbon electrodes. It is advisable to heat-treat their carbon electrodes before making supercapacitors. Studies show that supercapacitors with electrodes treated at 700  $^{0}$ C have a specific capacitance of C = 8.72 F/g and are about two times higher than supercapacitors made with non-heat-treated electrodes.

Keywords: thermal plasma, temperature, voltage, supercapacitor

#### **INTRODUCTION**

Nowadays, many industries, such as mobile phones, computers, transport, are facing increasing energy demand. Various batteries are commonly used as energy storage devices, but the major disadvantage is their loss of capacity after a certain number of charge - discharge cycles, which results in a reduction in their service life. The battery charging process also requires a reasonably long time. These energy storage devices also cannot form a large power pulse. The mechanism for accumulating the electrical charge of batteries is based on chemical processes, determining all the above-mentioned disadvantages. Batteries often use a variety of aggressive chemicals that are expensive and harmful to the environment (various acids, alkalis), as well as metals with limited resources (lithium) [1-4]. In search of an alternative to batteries, more and more attention is being paid to research on supercapacitors. The mechanism of charge accumulation in supercapacitors is not based on chemical processes but the effect of an electrostatic field [5]. The design of a supercapacitor is very similar to a conventional capacitor, but the supercapacitor can accumulate up to 2000 F/g. Since the mechanism of charge accumulation in supercapacitors is not based on chemical reactions, their number of chargedischarge cycles is practically unlimited. After one million charge-discharge cycles, the capacity is reduced by only about 5 %. Supercapacitors can also form a pulse of high-power electric current. In addition to all these advantages, supercapacitors also have a significantly lower cost than batteries and also have an almost unlimited life [6, 7-10]. Supercapacitors are classified into three main classes based on the materials used to make the electrodes: 1) Electrochemical Double Layer Supercapacitors (ESCs). Activated carbon, carbon aerogels, carbon nanotubes, etc. are used in their manufacture. 2) Pseudo-capacitors. They are made of transition metal oxides (the most widely used ruthenium oxide), conductive polymers polyaniline, polypyrrole, and others. 3) Hybrid capacitors. In their production, both activated carbon and metal hydrides are used. These capacitors have electrodes of different materials. Their properties include those of both ESCs and pseudo-capacitors [10-14].

The aim of this work is to evaluate the potential of plasma spraying technologies and their application in the field of supercapacitor electrode manufacturing. Design and produce a fully controllable microcontroller electronic system for supercharging and unloading supercapacitors for full automation that electrical capacitance measurements of supercapacitors.

# METHODOLOGY

A plasma generator (PG) (Fig. 1.) consisting of a copper (with a hafnium emitter) cathode (1), an insulating ring (3) and a stepped anode (2), supplied by high-temperature stable gas, was used for plasma flow generation and carbon coating streams. The anode chamber sections have lengths  $l_1$  and  $l_2$  of  $20 \cdot 10^{-3}$  and  $30 \cdot 10^{-3}$  m, and diameters  $d_1$  and  $d_2$  of  $2 \cdot 10^{-3}$  and  $4 \cdot 10^{-3}$  m. The electric arc is stabilized by working argon gas through the insulating ring into the arc zone. To obtain the required plasma flow rate, two inserts (G<sub>0</sub>) were introduced through the insulating ring to introduce argon gas. One hole  $10^{-3}$  m in diameter is drilled in the insulating ring for insertion of argon gas. Argon gas was used to inject the graphite powder. The powder was injected into the plasma generator anode region through an additional drilled hole in the anode (G1). More on all operation and management can be found in the literature [7].



Fig. 1. Plasma generator. 1 - cathode, 2 - anode, 3 - working gas injection ring, d - diameter, 1 - length.

Plasma sources arc current and voltage measurement, regulation and control are performed following the example of an ammeter and voltmeter. A tared shunt with an accuracy of 0.01 is used to measure the arc current. The arc current and voltage drop are measured with a digital ammeter and voltmeter DI3-72. Omega's FL-3439ST, FLDH3308G, and FL-3445C rotameter were used to measure argon gas flow. The FL-3439ST rotameter allows the gas flow to be adjusted from 0.94 to 14.13 l/min. The FLDH3308G rotameter allows the gas flow to be adjusted from 60 ml/min to 600 ml/min. o FL-3445C Rotameter 11.9 to 120.4 mL/min. The error of the Omega's rotameter shall not exceed 5% of the measured value and the repeatability shall be 0.25 %. The maximum operating temperature is 120  $^{\circ}$ C and a pressure of 13.8 bar. In order to improve the properties of the electrodes, was thermal treatment of the electrode material in the range of 100 - 900  $^{\circ}$ C temperatures was applied.

## **RESULTS AND DISCUSSION**

For the capacitance measurements and calculations, a classical capacitor charging and discharging stand was designed and manufactured, the electrical diagram of which is shown in Fig. 2.



The capacitor is charged to 5 V voltage using source of stabilized current, a constant resistor (18 k $\Omega$ ), a circuit-breaker connected to a pulse generator and forming a capacitor on-

off cycle, a capacitor under test and a digital multimeter (Agilent 34972A) connected to a computer. appropriate software to record the potential difference between capacitor electrodes. Figure 3 shows the time dependence of the charge current of the supercapacitors. As shown in the graphs, the charge peaks are symmetric, meaning that the charge time of supercapacitors does not depend on the number of charge-discharge cycles. During the charging process of the capacitor, the charging current is limited by 18 k $\Omega$  (Fig. 3) to 0.3 mA.



Fig. 3. Charging current of supercapacitors as a function of time.

This charge current is selected so that it is possible to capture the results of the voltage variations shown in Fig. 4.



Fig. 4. Charging voltage of supercapacitors as a function of time.

As we can see, the peaks of the voltage curve are symmetric, as are the currents (Fig. 4). The voltage charge peaks of supercapacitors with a higher specific capacitance are slightly wider, which is because a capacitor with a larger capacitance requires a higher charge time when the electric current is constant. It is also evident from the voltage charge diagrams that the formation of a galvanic pair is observed.

Due to the galvanic couple effect, the capacitors do not entirely discharge to zero voltage. Supercapacitors discharge approximately to 0.3 V. Studies show that supercapacitors with electrodes treated at 700 0C have a specific capacitance of C = 8.72 F/g.

# CONCLUSIONS

The charge-discharge cycles of supercapacitors show good repeatability of the chargedischarge peaks, so the number of charge-discharge cycles does not affect the material structure of the carbon electrode. The voltage charge peaks of supercapacitors with a higher specific capacitance are slightly wider, which is because a capacitor with a larger capacitance requires a higher charge time when the electric current is constant. It is also evident from the voltage charge diagrams that the formation of a galvanic pair is observed. Due to the galvanic pair effect, the capacitors do not discharge to zero voltage. Supercapacitors discharge to about 0.3 V. It is advisable to heat-treat their carbon electrodes before making supercapacitors. Studies show that supercapacitors with electrodes treated at 700  $^{\circ}$ C have a specific capacitance of C = 8.72 F/g and are about two times higher than supercapacitors made with non-heat treated electrodes.

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# METHODOLOGY AND ANALYSIS OF THE SEDIMENTATION VELOCITY OF FERROMAGNETIC PARTICLES IN MR LIQUIDS

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#### ABSTRACT

Magnetorheological fluids (MR fluids) are colloidal solutions, consisting of a carrier substance and active elements, which are ferromagnetic particles of iron (Fe), cobalt (Co), nickel (Ni) oxides. They are very small particles with dimensions not exceeding 10  $\mu$ m, polarized magnetically. Additionally, they are covered with a surface active agent (surfactant), which is oleic acid (C<sub>18</sub>H<sub>34</sub>O<sub>2</sub>), in order to prevent aggregation and sedimentation. MR fluids respond to changes in the intensity of the external magnetic field. A very important feature of the MR fluid is also the invariability of its parameters with respect to temperature. Nowadays, they are manufactured in such a way as to minimize the influence of temperature on the viscosity of the liquid, which they can operate at temperatures from -40°C to even 150°C. Due to the possibility of using MR fluids in the production of couplings, shock absorbers and vibration dampers, they are an interesting material for wider research.

One of the key parameters characterizing the MR liquid is the sedimentation rate of ferromagnetic particles. The aim of this study was to design and build a laboratory rig for measuring the velocity of falling particles (sedimentation) in MR liquids. The concept of the laboratory model was based on the design of an automated station, which included the following elements: PLC controller, SCADA system, RLC meter, measuring element (sensor) and the stand frame. The creation of such a research platform can significantly accelerate and facilitate the study of MR fluids. By using of the above-mentioned components, obtaining data and processing the results based on them will improve the work of future users of this rig. Moreover, the proposed solution is easy to use and can be quickly analysed.

Keywords: magnetorheological fluid, PLC, SCADA, sedimentation, velocity

#### **INTRODUCTION**

In recent years, there has been a continuous increase in interest in intelligent materials. Intelligent materials are structures whose properties can be changed appropriately as a result of an applied external stimulus. Among this type of materials, one can distinguish, inter alia, materials using piezoelectric, electrostrictive and magnetostrictive phenomena as well as shape memory phenomena [1]. Each group of intelligent materials has different characteristic properties that change under the influence of external stimuli. The changing property is a parameter that determines the application potential of material. Magnetorheological fluids (MRF), whose rheological properties change as a result of the applied magnetic field, are of great interest [2, 3]. MR fluids consist of three main components: magnetic particles, carrier fluid and appropriate additives. Ferromagnetic particles of iron (Fe), cobalt (Co), nickel (Ni) or their oxides are very often used as magnetic particles. Particular attention is paid to carbonyl iron, which is characterized by high magnetic properties. Mineral oil, engine oil as well as any low-viscosity synthetic oil are used as the carrier fluid. It is essential that the appropriate carrier fluid does not chemically react with the active particles. As additives, usually surfactants are used, whose task is to reduce agglomeration and sedimentation of magnetic particles. One of the commonly used additives are lithium stearate and ferrous oleate [4 - 6]. MRF respond to changes in the intensity of the external magnetic field. In the absence of forcing, the magnetic

molecules are not magnetized, so the total magnetic vector is zero. In such a case, the liquid retains the properties of an ordinary Newtonian fluid, which means that the tangential stresses  $\tau$  increase proportionally to the liquid deformation speed [7, 8]. Elementary particles of MRF placed in the area of the magnetic field become magnetized, so they can be considered as microscopic magnets [9]. Due to their unique properties, MRF are used in intelligent drive systems (clutches, brakes), damping systems (shock absorbers, vibration dampers and energy absorbers), as well as in surface treatment - magnetorheological polishing [10].

A significant limitation in the application of MRF is the agglomeration and sedimentation of magnetic particles. In order to select the appropriate additives limiting these processes, it is necessary to measure the MFR particle falling velocity. For this purpose, the most frequently chosen method is visual inspection during sedimentation observation. The determination of the particle falling velocity is based on the determination of the height of the liquid column as a function of time [11]. A visual assessment of sedimentation was presented by Aruna et al. [12], Zhang et al. [13] as well as Zhu [14].

Due to the problems related to the determination of sedimentation by the visual method (problems include low accuracy and repeatable results), the aim of this work was to design a test rig for measuring the falling rate of MFR particles. The assumption of the work was to automate the process allowing for more precise measurements. In addition, the creation of such a stand will significantly accelerate and facilitate the study of MRF. Thanks to the use of the developed system, data acquisition and the processing of results based on them will improve the work of future users of this platform.

#### METHODOLOGY

#### Material

In this project, used a MRF with 26% Fe particles content. The product was supplied by the LORD Corporation - MRF-126LF. It is a dark gray liquid with a viscosity (at 40°C) of about 0.07 Pa-s, with density of 2.68 g/cm3 and a solids content of 78% of the total volume.

#### Development of a test rig for measuring the sedimentation velocity of MRF particles

The concept of the laboratory model is based on the creation of an automated station, which includes the following elements: a PLC (Programmable Logic Controller - control over the entire process of the measurement), a SCADA system (Supervisory Control And Data Acquisition - allowing to visualize the operation of the executive system and displaying the collected data), an RLC meter (its advanced possibilities enable easy data acquisition and sanding data to SCADA), measuring sensor (innovative method of measuring MRF sedimentation - induction coil made of winding wire), station platform (supporting structure, where individual parts of the entire model can be embedded).

#### **Conducting sedimentation measurements**

All measurements were made on a MRF with 26% Fe particles content. The measuring cylinder was filled to 100 ml, which corresponds to approx. 200 mm in height. Measurement series were made in four time intervals (5h, 72h, 96h, 120h).

Based on the world literature on monitoring the state of MRF, which shows that the relative magnetic permeability is directly proportional to the concentration of MR liquid molecules, so that the inductance of the measuring sensor is also linearly dependent on the sedimentation of the MRF [13]. Due to this dependence, the MRF sedimentation rate is calculated based on the difference in inductance at individual time intervals.

# **RESULTS AND DISCUSION**

## Development of a test rig for measuring the sedimentation velocity of MRF particles

In the initial phase of the project, a computer model was created using the vector graphics editor - AutoCAD Inventor by AutoDesk, which facilitated the subsequent implementation of the entire structure. After making a sketch of the prototype, the next step was to make the measuring platform from pre-prepared elements. Fig. 1 shows the prototype and the actual form of the test rig for measuring the sedimentation of the MRF.



Fig. 1. Computer model versus real platform for liquid sedimentation measurement

The element responsible for controlling the entire measuring station is a PLC controller from the SIMATIC S7-1200 series, manufactured by Siemens. It is a fully programmable controller, used in many industries. The use of this element will allow to build an automatic system that will make the work on the platform will be fully autonomous in relation to the users.

The SCADA system was used to supervise the entire measurement process, through visualization, control, as well as archiving of the collected series of measurements. Thanks to the free software from Schneider Electric called IGSS FREE50, an intuitive system was created for measuring the sedimentation of MR liquids.

Another component used to build the measurement platform is the programmable RLC meter by Rohde & Schwarz – HM8118. It is a high-class device with a number of applications, as evidenced by as many as 14 possible measurement functions. By using a computer program whose algorithm enables automatic control of the HM8118 meter, a series of measurements can be carried out in a convenient way for the user. Fig. 2 shows the front panel of this application.

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Fig. 2. Hameg 8118 Control Program - application for remote control of the RLC meter

In this study, an innovative method measuring the sedimentation of MRF was used - induction coil as the sensor. The features identifying this solenoid are listed in Table 1.

Parameter	Value	Unit	
Number of turns	20	-	
Winding wire diameter	0,9	mm	
Coil inner diameter	45	mm	
Coil height	20	mm	
Inductance	20,8	μH	
Resistance	80	mΩ	

Table 1. Parameters of the inductive sensor

The measuring coil was placed in a specially designed frame, which was printed on a 3D printer. As a material was used PLA (polylactide), it has neutral properties in relation to the magnetic flux. An approximate view of this frame is shown in Fig. 3.



Fig. 3. Sensor frame

## **Conducting sedimentation measurements**

Fig. 4 shows how the velocity of liquid sedimentation changes in the distance domain for specific moments of time.



Fig. 4. Sedimentation rate of MR liquid

Based on the obtained results, it can be clearly stated that sedimentation is a nonhomogeneous phenomenon in the entire volume of the liquid and for different time intervals. By analyzing the above diagram, it is possible to identify individual areas of sedimentation. These areas along with their location are presented in Table 2.

Time internal Areas				Unit	
1 mie miervai	sediment	variable density	constant density	pellucid	mm
5h	0-35	35-75	75-100	100-160	mm
72h	0-35	35-70	70-120	120-150	mm
96h	0-25	25-60	60-100	100-130	mm
120h	0-20	20-75	75-100	100-140	mm

Table 2. Sedimentation areas for particular time intervals

# CONCLUSIONS

The aim of this project was to create a laboratory test rig for measuring the velocity of falling ferromagnetic molecules. The posted technical documentation, software and collected data testify to the positive implementation of the project topic.

The presented data clearly shows that with the passage time the boundaries of individual sedimentation areas change their location - this proves the correctness used measurement method.

The developed solution can be used in the future to test magnetorheological fluids applied in the production of couplings, shock absorbers and vibration dampers. The presented method allows to determine the sedimentation velocity of particles present in the tested liquid. The solution is easy to use and can be quickly analysed.

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# THE EFFECT OF THIN RECTANGULAR PLATE ON THE AERODYNAMIC DRAG OF A COMPACT SUV

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#### ABSTRACT

Efforts towards ever more energy efficient land vehicles have become one of the largest challenges of the automotive industry. Sports Utility Vehicles (SUVs) typically have a blunt rear end shape (for design and practicality); thus, suffer greatly from pressure (form) drag. Drag can be reduced by a number of passive and active methods such as tapering, passive vortex generators, and blowing into the base. Current experimental study investigates the effect of a passive flow control device, rectangular plates that introduced in the vicinity of lower and upper rear sides, on the drag of 1:10 scale compact SUV model. The simplified SUV model (Ero-cSUV) was designed by Authors. The proposed vehicle contains many of the features seen on a typical compact SUV. Furthermore, a SUV classification scheme was proposed by Authors. Experiments were performed in a closed-return, low-speed wind tunnel in the Department of Mechanical Engineering at the Munzur University. The tunnel has a 2.5 m long test section with cross-section 1 m high by 1 m wide. Experiments were conducted at freestream velocity of  $U_{\infty}$ =7.1 m/s, resulting in a Reynolds number of Re=176000 based on the length of the SUV model. The model, four cylindrical struts, plates and plate supports were printed by a 3-D printer. The effect of a range of plate heights (h), support lengths (g), and vertical distance between the ground and support (y) on the time-averaged and wind-averaged drag coefficients,  $\langle C_D \rangle$  and  $\langle C_D \rangle_{WA}$ , was assessed for  $-6^{\circ}$ ,  $-5^{\circ}$ ,  $-4^{\circ}$ ,  $-3^{\circ}$ ,  $-2^{\circ}$ ,  $-1^{\circ}$ ,  $0^{\circ}$ ,  $+1^{\circ}$ ,  $+2^{\circ}$ ,  $+3^{\circ}$ ,  $+4^{\circ}$ ,  $+5^{\circ}$ , and  $+6^{\circ}$  yaws ( $\gamma$ ). It is found that rear plates could reduce the  $\langle C_D \rangle_{WA}$  up to 6.1%. The optimum geometry comprises a flat plate with a height of h=30mm (h/H=0.221) placed 30 mm downstream (g/L=0.0706) of the model.

Keywords: SUV, Drag reduction, Passive flow control, Yaw angle, Rectangular plate

#### **INTRODUCTION**

Crossover (or crossover utility vehicle, CUV) is defined as "Typically wagon body style with unibody construction, front or all-wheel drive and passenger vehicle qualities being the dominant characteristic with limited off-road capability" [1]. A CUV is not a sport utility vehicle (SUV) in the literal sense. It is lighter and more fuel efficient than traditional SUV. However, it is a SUV-like vehicle, that is, tall, has higher ground clearance and seating position, has a largish cargo hold accessed through a rear door. At first glance, it is not easy to decide whether the vehicle is a CUV or a SUV; therefore, the term SUV will be used as a catch-all for both CUVs and SUVs throughout the paper.

Sport utility vehicle (SUV) popularity has increased significantly worldwide over the past two decades. It is reported that three out of 10 passenger vehicles sold in Europe, four out of 10 passenger vehicles sold in USA were SUVs [2].

There are many ways of classifying passenger vehicles (e.g. based upon interior volume index, curb weight, gross vehicle weight rating, etc.) even though it is generally not easy to compare the classification systems. Here, SUVs are divided into six size categories based solely on basic exterior dimensions (i.e. mini, small/subcompact, compact, mid-size, large-size, and full-size). Basic exterior dimensions ( $V_{BED} = \text{length} \times \text{width} \times \text{height}$ ) do not include the dimensions of extra parts such as roof rails, roof racks, roof box, external antenna, side-view mirrors, spare wheel mounted externally, etc. Only the 2020 and 2021 model year SUVs were

selected for classification. Reference  $V_{BED}$  ranges are determined by the technical similarities among considered SUVs (Table 1).

SUV size class	$V_{BED}$ (m <sup>3</sup> )	Examples
Mini	$V_{\rm PED} < 10.4$	Suzuki Jimny, Suzuki Ignis SZ5 4×4, Fiat Panda Cross
	V BED _ 10.1	etc.
Small (Subcompact)	$10.4 < V_{BED} \le 12.0$	Skoda Kamiq, Seat Arona, Audi Q2, Kia Stonic, Kia Xceed, Hyundai Kona, Dacia Sandero Stepway, Mazda CX-3, Renault Captur, Opel Crossland, Peugeot 2008, Ford Puma, Volkswagen T-Cross, Citroen C3 Aircross SUV, Suziki Vitara, Daihatsu Terios etc.
Compact	$12.0 < V_{BED} \le 13.4$	Skoda Karoq, Seat Ateca, Audi Q3, Toyota C-HR, Honda HR-V, Nissan Juke, Nissan Qashqai, BMW X1, BMW X2, Kia Niro, Dacia Duster, Renault Kadjar, Mazda CX-30, Opel Grandland X, Peugeot 3008, Volkswagen T-Roc, Mercedes EQA 250, Mercedes GLA, Ford Ecosport, Suzuki SX4 S-Cross, Fiat Egea Cross, Jeep Compass, Jeep Renegade, Mitsubishi Eclipse Cross, Subaru XV etc.
Mid-size	$13.4 < V_{BED} \le 16.5$	Skoda Kodiaq, Audi Q5, Toyota RAV4, Honda CR-V, Nissan X-Trail, BMW X3, Kia Sportage, Hyundai Tuscon, Mazda CX-5, Mazda CX-8, Peugeot 5008, Citroen C5 Aircross SUV, Volkswagen Tiguan, Volkswagen Tiguan Allspace, Volkswagen Touareg, Mercedes GLB, Mercedes GLC, Mercedes EQC Sport, Alfa Romeo Stelvio, Ford Kuga, SSangyong Korando, Range Rover Evoque, Range Rover Velar, Mitsubishi Outlander, Subaru Forester, Volvo XC40, Volvo XC60, Lincoln Corsair, Lincoln Nautilus etc.
Large-size	$16.5 < V_{BED} \le 18.5$	Audi Q7, Audi Q8, Toyota Land Cruiser Prado, BMW X5, BMW X6, Mazda CX-9, Mercedes GLE, Mercedes G-Class G 400, Land Rover Defender 90, Jeep Wrangler, Jeep Grand Cherokee, Volvo XC90, Lincoln Aviator etc.
Full-size	<i>V<sub>BED</sub></i> > 18.5	Toyota Sequoia, Nissan Armada, BMW X7, Mercedes GLS 400, Ford Expedition, Range Rover, Land Rover Discovery, Land Rover Defender 110, Chevrolet Suburban, Chevrolet Tahoe, GMC Yukon, Lincoln Navigator etc.

Table 1. SUV classification based on basic exterior dimensions ( $V_{BED}$ )

Hatchback and square-back shapes are popular designs in the SUV industry owing to their large cabin space and easy loading ability. However, the large rear surface area and associated wake are responsible for a significant proportion of the total aerodynamic drag acting on these vehicles. Therefore, some flow control methods which have the potential to reduce time-averaged drag were tested. For example, Varney et al. [3] investigated the basic aerodynamic effect of a range of body tapers and straight slots for 0° yaw. To this end, a 1/4 scale generic SUV model was used. It is stated that the best slot configuration reduce timeaveraged drag coefficient,  $\langle C_D \rangle$ , by 0.01, whereas the best taper configurations reduce  $\langle C_D \rangle$  by 0.035. Urquhart et al. [4] were numerically investigated the tapered rear end extensions with and without a kick for yawed flow conditions. A modified version of a Volvo XC60 AWD was used in their study. It is stated that the smooth extensions provide the greatest drag improvement at 0° yaw while the extensions with a kick yield additional benefits at yaw, effectively reducing

the vehicle's drag sensitivity to side wind. A multi-vehicle study (includes two SUV) was conducted by De Souza et al. [5] to quantify the aerodynamic drag changes associated with drag reduction technologies (i.e. active grille shutters, production and custom underbody treatments, air dams, wheel curtains, ride height control, side mirror removal, and combinations of them) for light-duty vehicles. Full scale test results suggest that active grille shutters, sealing the external grille, and ride height control reduce drag by redirecting incoming flow from the engine bay or underbody region to smoother surfaces above and around the vehicle. Littlewood and Passmore [6] investigated the effects of high aspect ratio roof trailing edge chamfer on the timeaveraged aerodynamic forces acting on the 1/4 scale simplified square-back model (Windsor model). It is stated that the optimum chamfer angle of 12° generates a significant drag savings of 4.4%. Furthermore, a reduction in time-averaged drag coefficient of 2.7% is achievable from only 4° chamfer configuration. Littlewood and Passmore [7] also investigated the effects of the steady blowing at the roof trailing edge of a simplified 1:4 scale square-back style vehicle (Windsor model) on the vehicle wake structures and the resulting body forces. Results show that overall gains can be achieved; however, the large mass flow rate required restricts the applicability of the technique to road vehicles. Sirenko et al. [8] investigated the effects of two passive flow control devices, rear screen which is plate behind the SUV and rear fairing, on the aerodynamic drag of the small-scale SUV of the General Motors. It is stated that rear screen could reduce time-averaged drag up to 6.5% and rear fairing can reduce the time-averaged drag by 26%. Gilliéron and Kourta [9] used a vertical splitter plates to reduce drag. This passive flow control method is similar to rectangular thin plates but they placed it at the rear or front of a simplified car/MPV geometry, not at the rear of a SUV.

The focus of the work reported in this paper is on the effect of thin rectangular plates which placed at various positions through the near-wake, are parallel to the lower (vertical) or upper (slanted) rear surfaces, attached firmly to the compact SUV model (Ero-cSUV) with a hollow circular cylinder (plate support). The effects of the dimensionless rectangular plate height (h/H), dimensionless gap between the plate and rear surfaces (g/L), and plate connection surfaces (i.e. Case A and B) is considered and result of force measurements are presented. There are some differences between this study and the study of Sirenko et al. [8]; frontal areas of the plates, shapes of the plates, and shapes of the SUVs are not same.

#### **EXPERIMENTAL SETUP**

Experiments were conducted in the closed-circuit wind tunnel in the Depatment of Mechanical Engineering at Munzur University. It has a working section 1000 mm wide 1000 mm high and 2500 mm long. The maximum freestream turbulence intensity  $(Tu_x)$  in the test section is 1%. Tunnel speed was measured with a handheld hot-wire anemometer upstream of the model. To minimize the effects of the floor boundary layer, a ground plane mounted on the tunnel floor in combination with a turntable and force measurement system. The gap between the bottom wall of the test section and ground plate was 100±0.2 mm. The leading and trailing edges of the ground plane are sharp. The front surface of the SUV model was located 120±0.7 mm downstream from the leading edge of the ground plate. The gap between the ground plate and the bottom of the SUV model was 23.8±0.2 mm. The model was supported by four cylindrical struts having a diameter of 8±0.2 mm. The distance from the sides of the SUV model to the centers of the struts was 40±0.7 mm. The distance from the front surface of the SUV model to the centers of the front struts and the distance from the rear surface of the SUV model to the centers of the rear struts were both equal to 86±0.7 mm. The 1:10 scale compact SUV model has a length, a width, and a maximum height of  $L=425\pm1$  mm,  $W=180\pm1$  mm, and  $H=136\pm1$  mm, respectively. The compact SUV model does not have side mirrors on it.

Experiments were carried out at maximum permissible freestream velocity of  $U_{\infty}=7.1\pm0.4$  m/s, resulting in a Reynolds number of  $Re=176000\pm9000$  based on the length of the SUV model. Therefore, we are not sure whether or not the SUV model is insensitive to Re above 176000. However, a literature review on time-averaged drag coefficients (i.e. dimensionless drag force),  $\langle C_D \rangle$ , of the 2020 and 2021 model year compact SUVs at zero yaw was conducted and it is found that they generally ranged from 0.31 to 0.35. The  $\langle C_D \rangle$  of the present model at zero yaw is 0.342±0.024; that is, this value is well within the range of  $\langle C_D \rangle$  of literature review.

Compact SUVs are enlarged hatchback-like vehicles. They generally have a rear diffuser, an arched roof, side surfaces whose upper parts inclined inward (tumblehome), and a rear-roof spoiler. Present SUV model (Ero-cSUV) also has a rear diffuser, an arched roof, and a rear-roof spoiler. All leading edges were well rounded to prevent separation. The rear slant angle was kept constant at  $45^{\circ}$ . The rear diffusor angle and length were kept constant at  $15^{\circ}$  and  $50\pm0.7$  mm, respectively. The uppest and lowest body surfaces of the SUV model is inclined inwards at an angle of  $21^{\circ}$  and  $3^{\circ}$ , respectively. CAD data of the SUV model is available from the first author on request.



Fig. 1. Schematic of the aerodynamic drag measurement system. Flow is from right to left.

Aerodynamic drag was recorded by one-component load-cell (ME-Meßsysteme GmbH, KD60-5N), which located under the test section of the tunnel (Fig. 1). The time-averaged drag acting on the struts and SUV model with and without thin rectangular plates,  $\langle F_D \rangle$ , was obtained by equation 1.

$$\langle F_D \rangle = \langle F_{DT} \rangle - \langle F_{DS} \rangle, \tag{1}$$

where  $\langle F_{DT} \rangle$  is the time-averaged drag acting on the components of the drag measurement system inside the test section, struts, and SUV model (N) and  $\langle F_{DS} \rangle$  is the time-averaged drag acting only on the components of the drag measurement system inside the test section (N). The aerodynamic drag was sampled at 200 Hz for 20 s (Marmatek Mesurement Technologies, VTA-1704). It was nondimensionalized (drag coefficient) using equation 2.

$$\left\langle C_D \right\rangle = \frac{2 \cdot \left\langle F_D \right\rangle}{\rho \cdot U_{\infty}^2 \cdot A_F} , \qquad (2)$$

where  $\rho$  is the air density (kg/m<sup>3</sup>) and  $A_F$  is the frontal area of the SUV model with struts (m<sup>2</sup>). The frontal area of the SUV model is 0.023924 m<sup>2</sup>. The effective blockage ratio for the test section (above the ground plane) is approximately 2.7%.  $\langle C_D \rangle$  values were not corrected for blockage effects since the effective blockage ratio is less than 5%. The uncertainty associated with the drag coefficient measurements is determined to be ±7%. For each plate configuration, force measurements were conducted at various yaw angles to allow the wind-averaged drag coefficient,  $\langle C_D \rangle_{WA}$ , which is the arithmetic mean of the  $\langle C_D \rangle$  values at yaws tested. The yaw angles tested range from -6±0.5° to +6±0.5° in 1° increments. The  $\langle C_D \rangle_{WA}$  has a percentage uncertainty of 10%.



Fig. 2. Schematic of and pictures of the rectangular plates (a) rigidly fixed to the center of the rear vertical surface and (b) rigidly fixed to the center of the rear slanted surface of the SUV model. Some geometric parameters were also given in the figure. The y/H values are 0.536 and 0.925, respectively, for cases A (left) and B (right).

To create the SUV model, struts, rectangular plates, and plate supports, three-dimensional (3-D) printer was used (Fig. 2). Three rectangular plates were used. The thicknesses, heights, and widths of the plates are  $2 \text{ mm} \times 30 \text{ mm} \times 60 \text{ mm}$ ,  $2 \text{ mm} \times 50 \text{ mm} \times 60 \text{ mm}$ , and  $2 \text{ mm} \times 70 \text{ mm} \times 60 \text{ mm}$ , respectively. The gaps between the planar rear surface of the SUV model and the rectangular plate are equal to the lengths of the plate supports which has a diameter of

 $10\pm0.2$  mm. The gaps tested range from  $10\pm0.2$  mm to  $50\pm0.2$  mm in 10 mm increments. Polyester putty and sandpapers with various grit sizes were used to make smooth model, plate, support, and strut surfaces. Then, SUV model was painted black.

#### **RESULTS AND DISCUSSION**

Results are given for two test cases (i.e. cases A and B). Each figure from 3 to 6 shows a comparison of the time-averaged drag coefficient,  $\langle C_D \rangle$ , for variations of yaw angles ( $\gamma$ ) and plate heights (h). Corresponding third order polynomial fits to the experimental data (solid lines) are given in the same figures. It must be noted that the degree of the polynomial fit causes a shift in the yaw angle where minimum drag is obtained.



Fig. 3.  $\langle C_D \rangle$  as a function of yaw angle for all dimensionless gaps (left). The solid curves represent the results from fitting the third order polynomials to the data. Case A. The height of the rectangular control plate is 30 mm (i.e. h/H=0.221).



Fig. 4.  $\langle C_D \rangle$  as a function of yaw angle for all dimensionless gaps (left). The solid curves represent the results from fitting the third order polynomials to the data. Case A. The height of the rectangular control plate is 50 mm (i.e. h/H=0.368).

As expected, the minimum  $\langle C_D \rangle$  is obtained at a yaw angle of around  $\gamma=0^\circ$ , irrespective of figure. The  $\langle C_D \rangle$  in Fig. 3 shows a slight decrease as g/L is increased for  $\gamma=0^\circ$ . Irrespective of the gap between the plate with h/H=0.221 and SUV model,  $\langle C_D \rangle$  of the SUV model with

rectangular plate is lower than that of the SUV model without rectangular plate except a few yaws. Increasing the rectangular plate height from h=30 mm to 50 mm (h/H=0.368) increased the minimum  $\langle C_D \rangle$  from 0.325 to 0.34, for  $\gamma=0^\circ$ . However, it is still lower than value of  $\langle C_D \rangle=0.342$  for the SUV model without plate. At  $\gamma=0^\circ$ ,  $\langle C_D \rangle$  drops slightly for increasing g/L until it reaches 0.34 at g/L = 0.0706. As the g/L is increased further,  $\langle C_D \rangle$  is increased and reached a maximum.



Fig. 5.  $\langle C_D \rangle$  as a function of yaw angle for all dimensionless gaps (left). The solid curves represent the results from fitting the third order polynomials to the data. Case A. The height of the rectangular control plate is 70 mm (i.e. h/H=0.515).



Fig. 6.  $\langle C_D \rangle$  as a function of yaw angle for two dimensionless gaps (left). The solid curves represent the results from fitting the third order polynomials to the data. Case B. The height of the rectangular control plate is 30 mm (i.e. h/H=0.221).

For h/H=0.515,  $\langle C_D \rangle$  drops sharply until reaching a minimum time-averaged drag coefficient of about 0.32 at g/L=0.0471 (Fig. 5). Further increase in g/L does not result in an improvement in  $\langle C_D \rangle$ .





For Case B, only one plate with a minimum height (i.e. h=30 mm) and two dimensionless gap distance between the SUV model and plate (i.e. g/L=0.0235 and 0.0471) were tested. This is done to prevent any increase in frontal area. It was concluded that rectangular plates attached to the slanted surface of the SUV have a negligible effect on  $\langle C_D \rangle$  (Fig. 6).

Fig. 7 shows a comparison of the wing-averaged drag coefficient,  $\langle C_D \rangle_{WA}$ , for various dimensionless gaps and rectangular plate heights (Case A). It is clear that SUV model with the smallest rectangular plate (i.e. h/H=0.221) performs best in terms of  $\langle C_D \rangle_{WA}$  reduction. This reduction reaches 6.1% as plate placed at g/L=0.0706. However, the mechanisms responsible for drag reduction were not clarified in the absence of some quantitative and qualitative techniques.

# CONCLUSION

Fuel consumption reduction is required for both economic and environmental reasons. Drag force have a great impact on the road vehicle fuel consumption.  $\langle C_D \rangle$  at the rear side of the compact SUV is, presumably, a major contributor to the total  $\langle C_D \rangle$  of it.

It is not reasonable or easy to associate any drop or increase in drag with the change in the wake flow structure without the aid of high fidelity numerical simulations, particle image velocimetry or flow visualization experiments. Therefore, the mechanism responsible for the improvement in drag performance is unclear.

The smallest rectangular plate (i.e. h=30) show the best performance in terms of windaveraged drag reduction (reduced by 6.1%). Attaching a rectangular plate to the rear lower (vertical) surface instead of the rear upper (slanted) surface seems to be more effective in reducing drag acting on compact SUV model. Rectangular plates attached to the lower rear surface (Case A) are effective tools not only for reducing drag at zero yaw but also for reducing the SUVs drag sensitivity to side wind.

#### ACKNOWLEDGEMENTS

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# CONFERENCE PAPERS

# **II.3.** Material sciences and technologies

F. I. Maxim et al. <u>PHOTOELECTROCHEMICAL DEGRADATION OF CARBON</u>
D N Moco et al THERMOEI ECTRIC PROPERTIES OF CO-DOPED TETRA HEDRITE
WITH NI OR CR, AND SE
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# PHOTOELECTROCHEMICAL DEGRADATION OF CARBON NITRIDES

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#### ABSTRACT

Polymeric carbon nitrides are metal free catalysts with high thermal and chemical stability which can be used in a variety of photo-catalytic reactions: water reduction and oxidation,  $CO_2$  reduction, degradation of organic pollutants from waste water, etc. This work focuses on the stability and the degradation mechanism of polymeric carbon nitride in photoelectrocatalytic conditions (i.e.,  $CO_2$ conversion). Polymeric carbon nitride (g-CN) was obtained by melamine thermic poly-condensation at 550°C. By further annealing of g-CN at 675°C under argon atmosphere red carbon nitride (g-CN-HT) was obtained. The composition and the structural characteristics of g-CN and g-CN-HT were assessed by elemental analysis, UV-VIS spectroscopy, FT-IR spectroscopy and transmission electron microscopy. We found out that the up-mentioned materials are prone to degradation at high overpotentials through a ring opening mechanism. This fact was confirmed by post mortem FT-IR analysis that showed for both samples the presence of -CH<sub>2</sub> groups and -N<sub>2</sub>C- bonds which highlighted the ring opening mechanism. Based on our finding we proposed a mechanism for the degradation of carbon nitrides.

Keywords: polymeric carbon nitride, CO<sub>2</sub> reduction, photo-electrochemical degradation

#### INTRODUCTION

The constant increase of carbon dioxide emissions, a greenhouse gas resulted from fossil fuels burning, represent a huge treat the environment as it leads to major global warming [1]. One of the factors in slowing these climate changes is to develop environment-friendly techniques for CO<sub>2</sub> capture, storage and conversion. As CO<sub>2</sub> conversion reaction to CO, COOH, etc. is both thermodynamically and kinetically unfavourable, it is crucial to develop cost-effective favourable catalysts for each possible reaction type: photocatalytic, electrocatalytic,

or photo-electrocatalytic [2, 3]. In this respect, during the past decade, various metal-based catalysts with expensive and time-consuming synthesis have been tested [4, 5, 6].

At the moment the research focuses on metal-free polymeric semiconductors such as carbon nitride due to its low cost, chemical stability, narrow band gap energy (2.7 eV) and appropriate conduction and valence band energies for  $CO_2$  conversion [7, 8]. However, the photoelectrochemical activity of pristine carbon nitride is rather low due to limited specific surface area, poor electron transfer ability and low visible-light absorption. To enhance its low activity towards  $CO_2$  photo-electro-reduction further enhancements are required: annealing, doping, constructing well-developed nanopores and inducing chemical modifications [9].

Polymeric carbon nitrides are a unique class of materials with a large number of nitrogen content. They are usually obtained from nitrogen rich precursors (i.e., melamine, cyanamide, etc.) through thermal poly-condensation techniques. The thermal poly-condensation product was considered to be the highly stable graphitic carbon nitride  $(g-C_3N_4)$ . However, this carbonnitrogen network is difficult to obtain by thermal treatment due to the existence of impurities present during the synthesis (i.e., hydrogen, oxygen) which produce changes to the ideal structure. Even though the structures are different, in literature they are still referred as graphitic carbon nitride.

Carbon nitrides were extensively tested for carbon dioxide reduction reaction (CO<sub>2</sub>RR) [22], however little is known about g-C<sub>3</sub>N<sub>4</sub> stability after the photo-electrochemical degradation. In this respect, we produced, using the thermal poly-condensation of melamine, two polymeric carbon nitrides: one synthesized at 550°C (g-CN) and another which annealed the g-CN at 675°C (g-CN-HT) aiming to study the photoelectrochemical degradation of CO<sub>2</sub> under visible light. We investigated the structural changes before and after photoelectrochemical degradation by employing elemental analysis, UV-VIS spectroscopy, FT-IR spectroscopy and transmission electron microscopy. We found out that the up-mentioned materials present irreversible structural transformation confirmed by the presence of the -CH<sub>2</sub> groups and -N<sub>2</sub>C- bonds in the post-mortem FT-IR analysis.

## METHODOLOGY

#### Reagents

Melamine (Sigma Aldrich, USA), ethanol (S.C. Tunic Prod S.R.L., Romania), NaHCO<sub>3</sub> (S.C. Herodio Crafts S.R.L., Romania) and Na<sub>2</sub>SO<sub>4</sub> (Chimactiv S.R.L., Romania) were used as received. Glass slides coated with a fluorine doped oxide (FTO) were supplied by Sigma-Aldrich (7  $\Omega$  cm<sup>-2</sup>, #735167-1EA, St. Louis, Missouri, USA). FTO glass was cut into 3cmx3cm pieces. Ultrapure water (> 18.2 M $\Omega$  cm) was produced by Milli-Q DirectQ System (Burlington, MA, USA).

#### g-CN and g-CN-HT synthesis

Polymeric carbon nitride (g-CN) was obtained by thermal poly-condensation of melamine for 4 hours at 550°C with a 5°C min<sup>-1</sup> heating rate. The reaction took place in a covered alumina crucible, in air, to prevent sublimation of melamine which takes place at equivalent temperatures as the thermal poly-condensation [10]. Further thermal treatment of g-CN for 4 hours at 675°C, under argon atmosphere, leads to the production of annealed carbon nitride (g-CN-HT) known as red carbon nitride. After the thermal process both samples were free cooled to room temperature.

#### **Carbon nitride film preparation**

Carbon nitride inks were prepared by dispersing 50 mg powder in 5 mL ethanol, followed by 15 min homogenized by means of an ultrasonic processor (Ultrasonics FS-250N, MXBAOHENG, Zhejiang, China). All carbon nitride films were produced by spraying the inks on heated FTO glass plates at 80°C by means of an air brush operated at 2 bar (HSENG, China, model AF186 Mini Air Compressor).

#### Structural and morphological characterization

Morphological characterization was performed with a transmission electron microscope (TEM: Tecnai G<sup>2</sup> F30 S-Twin, FEI-Philips, Hillsboro, OR, USA) operated at 300 keV). Ultraviolet-Visible analysis (UV-VIS) was conducted with a Jasco spectrophotometer (V550, Tokyo, Japan). FT-IR spectra were acquired on a Jasco FT-IR 6200 spectrophotometer (Acros Organics, USA) on IR grade KBr pellets. UV-VIS and FT-IR were used to assess the structural modification. Perkin Elmer analyser, model 2400 was used to determine the elemental composition of the up-mentioned materials.

#### **Electrochemical measurements**

Electrochemical measurements were performed employing a Voltalab electrochemical workstation (Voltalab, PGZ 301) connected to a photo-electrochemical cell (PECC-2, ZAHNER, Germany) equipped with a transparent working electrode with an 18 mm optical window diameter. Front illumination, with visible light, through the window was produced with a mercury lamp (PS-2, China). The three-electrode system used the various carbon nitride films as working electrodes, a platinum wire as counter electrode and Ag/AgCl reference electrode.

Polymeric carbon nitrides were tested for carbon dioxide reduction reaction (CO<sub>2</sub>RR) under visible light. Before the electrochemical measurements the PEC cell was filled with 0.1 M NaHCO<sub>3</sub> and purged with CO<sub>2</sub> for twenty minutes. The reduction photocurrents of each sample were measured under different potentials (-0.3 V, -0.4 V, -0.5 V, -0.6 V, -0.7 V). During each measurement 4 cycles of illumination/dark were performed (30 seconds dark and 30 seconds visible light). Due to the presence of carbonate ions that interfere in the FT-IR analysis, carbon dioxide reduction reaction experiments were repeated using 0.1 M Na<sub>2</sub>SO<sub>4</sub> electrolyte.

#### **RESULTS AND DISCUSSION**

The initial color of g-CN was yellow while the g-CN-HT color was red. Elemental analysis (CHN) showed that the C/N/H content is 35.5% carbon, 62.6% nitrogen and 1.1% hydrogen for g-CN and 35.8% carbon, 62.0% nitrogen and 0.7% hydrogen for g-CN-HT. The presence of hydrogen in both g-CN and g-CN-HT is due to the used precursor (melamine). The hydrogen loss in g-CN-HT due to the thermic treatment leads to the delocalization of electron in the heptazine hetorocycle. This fact is associated with the presence of the supplementary peak at 520 nm in the UV-VIS analysis (Fig. 2A). In comparison, the higher hydrogen content in g-CN is liked with the photoelectrochemical response (Fig. 3) where we can see that the maximum photocurrent density is obtained at ~0.6  $\mu$ A cm<sup>-2</sup>. The C/N ratio was 0.57 for g-CN and 0.58 for g-CN-HT, which is less than the C/N theoretical value for melon (0.67) and g-C<sub>3</sub>N<sub>4</sub> (0.75) [11, 12]. Both samples have similar structures which are closer to melon.

TEM investigation of g-CN revealed a polymeric morphology (Fig. 1A) with both disordered and well aligned and densely packed together structures. In contrast, g-CN-HT showed a graphitic like morphology without any visible ordering (Fig. 1B). g-CN-HT was
obtained at 675 °C which deformed the initial structure. Similar morphological features were encountered for red carbon nitrides [13, 14].



Fig. 6. Transmission electron microscopy of g-CN (A) and g-CN-HT (B)

Fig. 2A shows UV-VIS absorption spectra of g-CN and g-CN-HT. Both samples showed the specific feature of a semiconductor optical band gap: 2.60 eV for g-CN and 2.21 eV for g-CN-HT (estimated from Tauc and Mott-Schottky plots, data not shown). Similar value (2.7 eV) was reported in the literature for polymeric carbon nitride [15].



Fig. 7. The UV-VIS (A) and FT-IR spectra (B) of g-CN and g-CN-HT

g-CN showed only a peak at 370 nm while g-CN-HT showed an additional peak at 520 nm. g-CN's peak at 370 nm is given by the  $\pi$ - $\pi$ \* electron transition which explains the yellow colour. The source of the peak at 520 nm is considered to be the n- $\pi$ \* electron transitions involving lone pairs on the N atoms situated at the edge of the structure [5, 16]. Two peaks mean that g-CN-HT is a material which includes two components with slightly different structure. It should be mentioned that n- $\pi$ \* electron transitions are forbidden in ideal structures based on s-triazine repeating units [17, 18].

FT-IR spectroscopy (Fig. 2B) was used to assess the structure of polymeric carbonitrides [19, 20, 21]. The work of Komatsu [22] was used for peak identification. As we can see in Fig. 2B both samples showed a peak at 800 cm<sup>-1</sup>, specific for heptazine (i.e. cyameluric nucleus). An additional 6 peaks were identified in the 1200-1700 cm<sup>-1</sup> region which were attributed to different bonds in the heptazine heterocycle. The peaks at 1233 and 1350 were assigned to

trigonal nitrogen bonded to carbon atoms as in C-N(-C)-C. The 1403 and 1637 cm<sup>-1</sup> peaks correspond to the  $\delta$ (NH) and  $\delta$ (NH<sub>2</sub>), respectively. The bands at 1457 and 1571 cm<sup>-1</sup> correspond to the ring vibrations. The 2800 – 3400 cm<sup>-1</sup> region was assigned to v(NH).

Fig. 3 shows the absolute values of photocurrents obtained for photoelectrochemical CO<sub>2</sub> reduction. Both samples were tested between -0.3 and -0.7 V vs. Ag/AgCl. g-CN maximum photocurrent density was ~0.6  $\mu$ A cm<sup>2</sup> at an applied potential of -0.4 V, then the photocurrent density decreased to ~ 0.25  $\mu$ Acm<sup>2</sup> at -0.7 V vs. Ag/AgCl. The higher hydrogen content in the g-CN structure favours CO<sub>2</sub> reduction but the structure is unstable at more negative potentials. In contrast, g-CN-HT photocurrent density increased with the applied potential, obtaining a maximum photocurrent density of ~0.45  $\mu$ A cm<sup>2</sup> at an applied potential of -0.7 V vs. Ag/AgCl. For both samples the photocurrent density is smaller than 0.6  $\mu$ A cm<sup>2</sup>. In literature the reported values of photocurrent density varies from 0.1  $\mu$ A cm<sup>2</sup> to 10  $\mu$ A cm<sup>2</sup> [16, 23, 24, 25]. As we can see in Fig. 3 g-CN-HT maximum photocurrent density is smaller than that obtained for g-CN. This fact is associated with the carbon nitride thermic treatment (675°C) which leads to a less hydrogen content in the material structure, but to a more stable structure at negative potentials. In the long run, g-CN-HT is more stable than g-CN at negative potentials, but more unfavorable to CO<sub>2</sub> reduction.



Fig. 8. Absolute values of the photocurrents obtained from CO<sub>2</sub>RR experiments under visible light

The structure of g-CN and g-CN-HT after photo-electrochemical CO<sub>2</sub>RR experiments was investigated with FT-IR. The investigation is known as post-mortem analysis. The electrolyte used in the experiments was 0.1 M Na<sub>2</sub>SO<sub>4</sub> due to fact that sodium sulphate has 2 absorption bands at approx. 600 and 1100 cm<sup>-1</sup> that does not interfere with carbon nitride absorption bands in IR. Fig. 4 shows FT-IR results for initial (black curves) and post-mortem (red curves) g-CN (Fig. 4A, 4B and 4C) and g-CN-HT (Fig. 4D, 4E and 4F). The FT-IR spectra were normalized to the largest feature (i.e. 1233 cm<sup>-1</sup>). There were three region of interest: (1) the 2000 – 4000 cm<sup>-1</sup> region specific for adsorbed water and amines (Fig. 4A and 4D), (2) the 1000 – 2000 cm<sup>-1</sup> region specific for heterocycle vibrations (Fig. 4B and 4E) and (3) the 950 - 1050 cm<sup>-1</sup> region specific for -N<sub>2</sub>C- bonds (Fig. 4C and 4F).



Fig. 9. FT-IR normalized transmittance of initial (black curves) and post-mortem (red curves) of g-CN and g-CN-HT. Blue circles in A and D shows the methylene (-CH<sub>2</sub>-) specific vibration at 2853/2922 cm<sup>-1</sup>. The blue circles in C and F shows 985/1005 cm<sup>-1</sup> peak assigned to -N<sub>2</sub>C- bond. The red curves in A, C, D and F are y-offset by -0.1

The 2000 – 4000 cm<sup>-1</sup> region shows, a peak at 3450 cm<sup>-1</sup> specific for OH bond, another three peaks between 3000 - 3300 cm<sup>-1</sup> specific for amines and a doublet at 2853/2922 cm<sup>-1</sup> and 2852/2922 cm<sup>-1</sup> specific for methylene v(-CH<sub>2</sub>-). Another doublet assigned to the CO<sub>2</sub> gas present in the FT-IR testing chamber is shown at 2450 cm<sup>-1</sup>. For post-mortem samples the peak assigned to OH bond is bigger than that of initial samples. The increase can be explained by the water adsorbed on the surface during photo-electrochemical degradation experiments and as a part of the material structure acquired during thermal synthesis. The amines peaks are smaller than that of initial samples meaning that the structure is slightly different. The methylene peaks do not appear in the initial samples, which is in accordance with the literature which state that C-H bonds are forbidden in the heptazine based carbon nitride and melon theoretical model [26, 27].

The  $1000 - 2000 \text{ cm}^{-1}$  region shows seven peaks which are attributed to heterocycle vibration. The peaks from 1250 to 1650 cm $^{-1}$  does not show difference between initial and postmortem samples. The peak at 1206 cm $^{-1}$  which is specific for C-O bonds showed a slight increase in transmittance for post mortem samples in comparison with initial samples. The presence of oxygen moieties in the initial structure is due to reaction condition. The reaction took place in a covered crucible, in air (see Section 2.2).

The  $950 - 1050 \text{ cm}^{-1}$  region shows another difference between initial and post-mortem samples. The existence of the 990-995 cm<sup>-1</sup> adsorption band is assigned to the -N<sub>2</sub>C- bond [28].

Elemental analysis showed that the initial structure of g-CN and g-CN-HT are similar in composition and closer to melon structure than that of graphitic  $C_3N_4$ . Fig. 5 shows the melon structure (Fig. 5A) and the possible structure of the degraded carbon nitrides (Fig. 5B). As can

be seen in the post mortem FT-IR spectra the peaks associated with the nitrogen bonded to the three carbons at the heptazine's core (Fig. 4B and Fig. 4E) remain unchanged after the photoelectrochemical degradation. Another modification is observed in the 3000 to  $3350 \text{ cm}^{-1}$  region, where the peaks associated with the amines are smaller than those obtained before photoelectrochemical degradation. These peaks are associated with the primary amines at the margins of the polymeric network (N=C(-NH<sub>2</sub>)-N), and the secondary amines linking C-(NH)-C units. After degradation, when heptazine unit loses at least 2 amines, by partly losing its C=N bonds, it will open one of the rings. This results in a methylene terminal (-CH<sub>2</sub>). The degradation mechanism of carbon nitrides by heptazine ring opening is confirmed due to the methylene peaks (Fig. 4A and Fig. 4D) and by the peaks assigned to the -N<sub>2</sub>C- bonds ( 990-995 cm<sup>-1</sup>) (Fig. 4C and Fig. 4F) shown in the post-mortem samples.



Fig. 10. Melon (A) and the possible structure of the degraded carbon nitrides (B): carbon (black), hydrogen (white), nitrogen (blue) and oxygen (red). Structures were created with Hyperchem software.

## CONCLUSIONS

Polimeric carbon nitride (g-CN) was synthesized by thermal polycondensation of melamine. g-CN-HT known as red carbon nitride was obtained from annealed g-CN. Both materials were tested for photoelectrochemical  $CO_2$  reduction in order to investigate their degradation mechanism. During the photoelectrochemical  $CO_2$  reduction the material showed irregular photocurrent trends. In the long run g-CN-HT is more stable between the two, although the photoecurrent density is smaller than that of g-CN.FT-IR post-mortem analysis reveals irreversible structural transformation emphasized by the presence of methylene groups (-CH<sub>2</sub>) and carbon atoms bonded to two nitrogen atoms (-N<sub>2</sub>C-). Such chemical bonds are forbidden in the ideal structure of carbon nitrides. Based on our findings we proposed a degradation mechanism of carbon nitrides by heptazine ring opening (Fig. 5B). As far as we know no report in the literature proposed a ring opening as a degradation mechanism of carbon nitrides during photoelectrochemical  $CO_2$  reduction. We believe that our finding can open new possibilities in the carbon nitride based catalyst.

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## THERMOELECTRIC PROPERTIES OF CO-DOPED TETRAHEDRITE WITH NI OR CR, AND SE

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#### ABSTRACT

The current thermoelectric materials with commercial applications are produced with expensive and/or toxic elements, such as the Bi, Pb and Te, amongst others. A potential alternative to this problem is the application of a mineral called tetrahedrite (Cu<sub>12</sub>Sb<sub>4</sub>S<sub>13</sub>), which is composed of earth-abundant elements with lower toxicity, displays good electrical and thermal properties that permit a zT of 0,6 at 700K. This value is still too low when compared with current commercial thermoelectric devices (with zT> 1,0), but, as it has been proved by several studies, it can be increased with isovalent doping. The focus of this project has been the studying the effect of two simultaneous isovalent doping in tetrahedrite properties, following the composition Cu<sub>12-x</sub>M<sub>x</sub>Sb<sub>4</sub>S<sub>13-y</sub>Se<sub>y</sub>, where M=Ni, Co or Cr. At the present stage, the X-ray diffractograms have shown that all samples have a main tetrahedrite phase with a small presence of other phases after annealing at 723K for 7 days, and some samples have the potential of manifesting a high thermoelectric efficiency including one with theoretically estimated zT=0,32 at 300K.

Keywords: Tetrahedrites, as-cast materials, annealed materials, thermoelectric materials, power factor

## **INTRODUCTION**

No transformation processes important for humans are capable of full energy conversion into the desired output, all being plagued with losses in the form of noise, by-products, radiation, or heat. From automobile engines to power plants, these losses are so rampant in energy production processes, both renewable and non-renewable, that often less than a third of the total energy produce is usable, the remaining coming mostly as waste heat.[1–3]

To mitigate these losses, waste heat can be harvested to produce electricity using thermoelectric generators (TEG).[4] These devices require a particular set of semiconducting materials (n- and a p-type) that manifest the thermoelectric phenomena in a strong or employable way, thus capable of generating high enough voltages over a series of small n-type and a p-type modules assemble in series. [5,6]

The measure by which the potential of thermoelectric materials is compared is the figure of merit, zT, a dimensionless number, which is calculated by the formula:

$$zT = T.S^2/(\rho.\kappa),\tag{1}$$

where T represents temperature, S represents Seebeck coefficient,  $\rho$  represent electrical resistivity and  $\kappa$  represents thermal conductivity. There are several materials already

commercially available that possess high zT (>1), but the majority of them require rare, expensive and/or toxic elements such as Pb, Bi and Te.[7–10] Thus, there is a call for novel materials that are less expensive and toxic, and possess zT $\geq$ 1. [11]

One potential candidate is tetrahedrite (Cu<sub>12</sub>Sb<sub>4</sub>S<sub>13</sub>), which is a natural and worldwide abundant sulfosalt mineral. The name derives from the distinctive tetrahedron-shaped crystals formed by complex body centred cubic unit cells, space group I4  $\overline{3}$ m (217), with 58 atoms per unit cell and five crystallographic positions (Cu (12*d*), Cu (12*e*), Sb (8*c*), S (2*a*) and S (24*g*)).[12–14] The good thermoelectric properties of tetrahedrites derive from a very-low thermal conductivity, which has been connected to the low-energy vibration of Cu (12*e*) located inside a S3 triangle plane.[11,13,15] That results in a zT=0.7 at 623 K [12,13,16], which can be tuned by chemical substitution (doping), with some studies reporting figure of merits as high as 1,0.[17]

Partial substitution of copper with nickel, cobalt and chromium, as well as, sulphur with selenium, have been reported to increase thermoelectric properties, [17–27] but few studies have been conducted regarding multiple substitutions. Thus, the present paper describes the impact on the Seebeck coefficient and electrical resistivity of double substitutions, of Copper with Nickel and Sulphur with Selenium, as part an ongoing project to study other dopants (Cobalt and Chromium).[26,28] X-ray diffraction, Raman Spectroscopy and Scanning Electron Microscopy (SEM) were used to characterize the samples at the various stages of sample preparation.



Fig. 1. Crystalline structure of Tetrahedrite[12]

#### EXPERIMENTAL

Cu<sub>12-x</sub>Ni<sub>x</sub>Sb<sub>4</sub>S<sub>13-y</sub>Se<sub>y</sub> ( $0 \le x \le 1,5$ ;  $0 \le y \le 1,5$ ) samples and Cu<sub>12-z</sub>Cr<sub>z</sub>Sb<sub>4</sub>S<sub>13-y</sub>Se<sub>y</sub> ( $0 \le z \le 0,5$ ;  $0 \le y \le 1,5$ ) samples were synthesized by reacting the pure elements (Cu (99,99%), Ni (99,99%)), Cr (99,99%), Sb (99,99%), S (99,99%), Se (99,99%)) inside quartz ampoules sealed under vacuum ( $10^{-1}$  Torr). Each element was weighed to match the stoichiometric ratio of the formula in each sample and an excess of sulphur was added in an effort to offset losses due evaporation, approximately 1,0 wt% of the amount weighed for each sample. The samples were submitted to a casting process with multiple steps: (I) were heated to 1173K at the rate of 4 K/min and kept at that temperature for 1 hour, (II) then cooled to 973K at the rate of 11 K/min kept for 10 minutes, after which (III) were cooled to 923K at the rate of 11 K/min kept for 20 minutes and finally (IV) cooled to 673K the rate of 4K/min kept for 18 hours before being removed from the oven. An annealing step was also underwent, after casting, the samples were crushed in a mortar into a fine powder, which was shaped into disks by cold pressing with a hydraulic press. The disks were then sealed under vacuum ( $10^{-1}$  Torr) inside quartz ampoules and subjected to a temperature treatment at 723K for 7 days.

After the casting and annealing, a small portion of each sample was crushed manually into a fine powder to be characterized by X-ray diffraction and Raman spectroscopy. The X-ray diffraction was performed on D2 Phaser Bruker 2nd Gen, by measuring in the  $10^{\circ}$ -  $65^{\circ}$  interval, with a  $0.02^{\circ}$  step and taking 0.6 seconds per step, through 1.0mm slit. The Raman

spectroscopy was carried out with the LabRAM HR Evolution Raman Spectrometer. The PowderCell package, Diffrac.EVA, Origin 90E and UnitCell software were used to analyse the data and calculate the lattice parameter of the samples.

Another portion of the samples (after casting and annealing) were manually polished with SiC paper, in order to be analysed with SEM combined with Energy-Dispersive Spectroscopy (EDS) using a JEOL JSM-7001F field emission gun scattering electron microscope, equipped for EDS with Oxford light elements detector.

The measuring of the electrical resistivity and Seebeck coefficient of the samples was made in the 20-350K temperature range, by employing a modified version of the method employed by Chaikin,[29] in order to by applied to inorganic samples. Two pieces were removed from the annealed samples, a needle-like shaped piece  $(2x0,5x0,5 \text{ mm}^3)$  for the Seebeck coefficient measurements and a cuboid/flat prismatic shaped piece  $(2x1,5x0,5 \text{ mm}^3)$  for the electrical resistivity measurements. The resistivity is measured with standard four-probe method with silver paint electrical contacts. As for the Seebeck effect, the piece is glued to two sheets of gold which are glued to two bars of quartz connected to gold probes coated with silver paint.



Fig. 2. (A) X-ray diffractograms (diamonds identify peaks of secondary phases) and (B) Raman Spectra (triangles indicate tetrahedrite) of as-cast  $Cu_{12-x}Ni_xSb_4S_{13-y}Se_y$  samples.







Fig. 4. X-ray diffractograms of annealed Cu<sub>12-x</sub>Ni<sub>x</sub>Sb<sub>4</sub>S<sub>13-y</sub>Se<sub>y</sub> samples, marked with diamonds are peaks belonging to secondary phases.

#### RESULTS

#### X-ray Diffraction and Raman Spectroscopy

Figures (2, 3 and 4) show the diffraction patterns of the samples after casting and annealing of both dopant combinations:  $Cu_{12-x}Ni_xSb_4S_{13-y}Se_y$  and  $Cu_{12-z}Cr_zSb_4S_{13-y}Se_y$ , where x=[0; 0,5; 1,0; 1,5], y=[0; 0,5; 1,0; 1,5] and z=[0; 0,1; 0,3; 0,5]. Overall Ni-Se samples and Cr-Se samples, yield very similar diffractograms and spectra.

In the diffractograms, the most intense peaks are congruent with the tetrahedrite structure (I4 $\overline{3}$ m, space group number 217), indicating that even after casting the samples are mainly tetrahedrite. However less intense peaks are also observed, mostly in as-cast samples. These peaks are indicative of secondary phases, the most common being stibnite (Sb<sub>2</sub>S<sub>3</sub>), covellite (CuS) and chalcostibite (CuSbS<sub>2</sub>). It is also important to notice that after annealing the presence of secondary phases peaks are less frequent and, when observed, are much less intense. This indicates that despite the current casting procedure being able to samples with a major tetrahedrite phase, the annealing step is still important to mitigate secondary phases.

The interpretation of the Raman spectra also provided similar insight into the secondary phases and served to confirm that tetrahedrite is the main phase in all the samples. There was some doubt regarding the presence of skinnerite which has a signature pattern similar to tetrahedrite, however the most intense of the pair of signature peaks is located in the 348 cm<sup>-1</sup> shift rather than the 315cm<sup>-1</sup>, which is specific to tetrahedrite.[30,31]

The relation between dopant content and the lattice parameters of the tetrahedrite phase was studied and represented in Fig. 5, 6, 7 and 8. The lattice parameter ranges between 10,314-10,404 Å and, has shown in Fig. 5 and 6, the variations tend to be small with changes in Nickel content. This is due to the small difference between the ionic radius of  $Cu^{2+}$  (73 pm) and Ni<sup>2+</sup> (69 pm). On the other hand, lattice parameter tends to increase with Se content, as the ionic radius of Se<sup>2-</sup> (198 pm) is appreciably larger than S<sup>2-</sup> (184pm). Another observation is that it seems to exist a slight tendency for the lattice parameter to increase after annealing (Fig. 7) suggesting that more dopant (particularly Se) is being integrated into the tetrahedrite phase.

It is important to mention that, at the time of this submission, the Cr-Se characterization was still undergoing and some samples have not been studied (their values are missing). However, it was noticed that, similarly to Ni doped samples, variations in Cr-content in the sample produce very small changes in the lattice parameter which is also related to the small difference in ionic radius between  $Cr^{2+}$  (80 pm) and  $Cu^{2+}$  (73 pm).



Fig. 5. Lattice parameter dependence on Nickel content (x) and Selenium content (y) in ascast  $Cu_{12-x}Ni_xSb_4S_{13-y}Se_y$  samples



Fig. 6. Lattice parameter dependence on Nickel content (x) and Selenium content (y) in annealed Cu<sub>12-x</sub>Ni<sub>x</sub>Sb<sub>4</sub>S<sub>13-y</sub>Se<sub>y</sub> samples



Fig. 7. Lattice parameter dependence on total dopant content (x+y) in as-cast (circles) and annealed (squares) Cu<sub>12-x</sub>Ni<sub>x</sub>Sb<sub>4</sub>S<sub>13-y</sub>Se<sub>y</sub> samples.



■ 10,3-10,32 ■ 10,32-10,34 ■ 10,34-10,36 ■ 10,36-10,38 ■ 10,38-10,4 ■ 10,4-10,42

Fig. 8. Lattice parameter dependence on Chromium content (z) and Selenium content (y) in as-cast Cu<sub>12-z</sub>Cr<sub>z</sub>Sb<sub>4</sub>S<sub>13-y</sub>Se<sub>y</sub> samples.

#### Scanning Electron Microscopy and Energy-Dispersive Spectroscopy (SEM-EDS)

SEM images of the samples are presented in Fig. 9 and the measured composition of the phases (EDS) is shown on table 1.

In the case of Ni and Se doped samples, SEM-EDS displayed a matrix with atomic composition very similar to tetrahedrite with a small content of Ni and Se, in agreement to the expected composition of each sample, proving that chemical substitution with Ni and Se is occurring. However, a common occurrence in as-cast samples doped with nickel, is the formation of dendritic nickel sulfides (Ni<sub>x</sub>S<sub>y</sub>) with a small presence of Cu and Se, generally less than 5,0 at% each. Samples doped only with Selenium and the Cu<sub>10,5</sub>Ni<sub>1,5</sub>Sb<sub>4</sub>S<sub>11,5</sub>Se<sub>1,5</sub> composition, also manifest a lighter-shaded phase with the atomic content similar to chalcostibite doped with Se, which seems to be related to the presence of Se in the sample. However, in the presence of Ni chalcostibite is not observed, with the single exception being the Cu<sub>10,5</sub>Ni<sub>1,5</sub>Sb<sub>4</sub>S<sub>11,5</sub>Se<sub>1,5</sub> sample that manifests small quantities of both nickel sulfide dendrites and chalcostibite, which is most likely related to the large combined amount of dopants. Therefore, two things can be inferred from the SEM-EDS analysis: i) Se-doping favors the formation of chalcostibite; ii) Ni-doping favors the formation nickel sulfide dendrites and prevents the chalcostibite phase.

Ni doping seems to increase the tetrahedrite content in the sample, seemingly stabilizing it. On a side note, the sample without any doping produced two different tetrahedrite phases. As the second tetrahedrite microstructure is not observed in any other sample, Ni and Se dopants seem to prevent the formation of multiple tetrahedrite phases at the casting step. Overall, ascast samples always manifested at least one extra phase, either the nickel sulfide or the chalcostibite, with the sample  $Cu_{10,5}Ni_{1,5}Sb_4S_{11,5}Se_{1,5}$  manifesting both.

After annealing, the results indicate an increase in the estimated tetrahedrite content (>94 at%) and half of the samples do not manifest any other phase, indicating that annealing is an important step to obtain samples with more accurate results in the measurements of thermoelectric properties.

In the case of Cr and Se doped samples after casting, SEM-EDS analysis also displayed a tetrahedrite-matrix, but without traces of Cr in all of the them. In fact, Cr is only found in needle-like formations of copper-chromium sulfide (CuCrS<sub>2</sub>). The copper-chromium sulfide remains present even after annealing, as it can be seen in Fig. 9. This means that chemical substitution of Cu for Cr is not occurring in the as-cast materials prepared by the current synthesis process and, consequently, such samples were not further analyzed and the annealed samples will be further characterized.



Fig. 9. SEM images of (A) As-cast Cu<sub>10,5</sub>Ni<sub>1,5</sub>Sb<sub>4</sub>S<sub>11,5</sub>Se<sub>1,5</sub> sample, with the lighter toned CuSbS<sub>2</sub> phase and the dark NiS dendrites; (B) Annealed Cu<sub>10,5</sub>Ni<sub>1,5</sub>Sb<sub>4</sub>S<sub>11,5</sub>Se<sub>1,5</sub> sample with a dark toned NiS phase; (C) As-cast Cu<sub>11,5</sub>Cr<sub>0,5</sub>Sb<sub>4</sub>S<sub>13</sub> sample with a needle-like CuCrS<sub>2</sub> phase; and (D) Annealed Cu<sub>11,5</sub>Cr<sub>0,5</sub>Sb<sub>4</sub>S<sub>13</sub> sample with a CuCrS<sub>2</sub> phase.

Table 1. Nominal composition, measured composition (EDS) and secondary microstructures of  $Cu_{12-x}Ni_xSb_4S_{13-y}Se_y$  samples and  $Cu_{12-z}Cr_zSb_4S_{13-y}Se_y$  samples. Measured composition is determined after normalizing for a 29 atoms molecule.

Nominal composition	Synthesis stage	Measured composition (EDS)	Secondary microstructures	
$Cu_{10,5}Ni_{1,5}Sb_4S_{11,5}Se_{1,5}$	As-cast	Cu <sub>12,8</sub> Ni <sub>1,6</sub> Sb <sub>4,1</sub> S <sub>8,5</sub> Se <sub>2,0</sub>	NiS and CuSbS <sub>2</sub>	
Cu10,5Ni1,5Sb4S11,5Se1,5	Annealed	$Cu_{10,9}Ni_{1,3}Sb_{4,0}S_{11,7}Se_{1,1}$	NiS	
$Cu_{11,5}Ni_{0,5}Sb_4S_{12}Se_1$	As-cast	Cu <sub>13,6</sub> Ni <sub>0,5</sub> Sb <sub>3,8</sub> S <sub>10,1</sub> Se <sub>0,9</sub>	NiS <sub>2</sub>	
Cu11,5Ni0,5Sb4S12Se1	Annealed	$Cu_{11,4}Ni_{0,6}Sb_{4,0}S_{12,2}Se_{0,8}$	-	
Cu <sub>11,5</sub> Cr <sub>0,5</sub> Sb <sub>4</sub> S <sub>13</sub>	As-cast	$Cu_{14,9}Sb_{4,0}S_{10,1}$	CuCrS <sub>2</sub>	
$Cu_{11,5}Cr_{0,5}Sb_4S_{13}$	Annealed	Cu <sub>12,2</sub> Sb <sub>4,3</sub> S <sub>12,5</sub>	CuCrS <sub>2</sub>	

## Seebeck Coefficient and Electrical Resistivity

The temperature dependence of the Electrical resistivity ( $\rho$ ) and Seebeck coefficient (S) of the Cu<sub>12-x</sub>Ni<sub>x</sub>Sb<sub>4</sub>S<sub>13-y</sub>Se<sub>y</sub> samples after annealing are shown in Fig 10, and the electrical resistivity, Seebeck coefficient, estimated thermal conductivity, and calculated power factor (PF) and figure of merit at 300K are presented in table (2).

The electrical resistivity of the materials tends to increase as the temperature decreases, which is a characteristic of semiconductor behavior, and the Seebeck coefficient is always positive indicating that "holes" are the main charge carriers making tetrahedrite a p-type semiconductor. The fact that Seebeck coefficient decreases as temperature decreases, indicative of metallic behavior, points to tetrahedrites with a highly degenerate semiconducting behavior. It is also noted that the two samples whose compositions have been previously studied (Cu<sub>10,5</sub>Ni<sub>1,5</sub>Sb4S<sub>13</sub> and Cu<sub>12</sub>Sb4S<sub>13</sub>), the temperature dependence of electrical resistivity and Seebeck coefficient are very similar to the described in those works, albeit the overall Seebeck coefficient values are slightly lower than the reported.[13,32–36] This difference is most probably because the reported studies were made on materials that were only annealed. This means that our samples should have higher porosity, cracks and other structural imperfections that have a detrimental effect on the thermoelectric properties.

In general, electrical resistivity and Seebeck coefficient tends to increase with Ni content, which is congruent with other studies.[13,27] This increase is caused by a shift of the Fermi level to the top of the valence band, which causes a decrease in carrier concentration, thus increasing Seebeck coefficient and electrical resistivity. Regarding the Se content, studies have shown that there is an increase of electrical resistivity with Se content in tetrahedrite up to y=1,0 after which the electrical resistivity increases but remains below undoped tetrahedrite.[34] As for Seebeck coefficient, it is reported to increase almost linearly with Se-content. In the present results, samples with small amounts of dopant (Cu<sub>12-x</sub>Ni<sub>x</sub>Sb<sub>4</sub>S<sub>13-y</sub>Se<sub>y</sub> samples where x+y $\leq$ 1,5) display the expected decrease in electrical resistivity and increase in Seebeck coefficient. However, with higher dopant content, in particular the curves for Cu<sub>10,5</sub>Ni<sub>1,5</sub>Sb<sub>4</sub>S<sub>13-y</sub>Se<sub>y</sub>, there is a massive increase from y=0 to y=0,5, in electrical resistance and Seebeck coefficient that does not exhibit the almost linear relation (Fig. 11).

In terms of Power Factor (PF), which is calculated through the formula

$$PF = S^2/\rho, \tag{2}$$

the Ni-content in tetrahedrite despite increasing both electrical resistivity and Seebeck coefficient, lowers the PF of the materials and is presumed to achieve a maximum PF with x=0,5, due to the increase in electrical resistivity exceeding that of the Seebeck coefficient. As for Se-content, which decreases electrical resistivity up to y= 1,0 and increases Seebeck coefficient, is expected to achieve a maximum PF at y=1,0. The results have shown, however that the maximum PF achieved at 300K was of PF=1277,73  $\mu$ W/m.K<sup>2</sup> for the sample Cu<sub>11,5</sub>Ni<sub>0.5</sub>Sb<sub>4</sub>S<sub>12,5</sub>Se<sub>0.5</sub>. This lead us to prepare a new sample with the same composition for confirmation, which although only wielded a PF=212,43  $\mu$ W/m.K<sup>2</sup>, is still a rather high. The second highest PF was achieved for the sample Cu<sub>11,5</sub>Ni<sub>0,5</sub>Sb<sub>4</sub>S<sub>12</sub>Se with a PF=335,63  $\mu$ W/m.K<sup>2</sup>.

Although the thermal conductivity will still be measured, an early estimation of the  $\kappa_T$  was made in order to determine the zT at 300K. The calculation of the thermal conductivity was carried out by the formula:

$$\kappa_T = \kappa_L + \kappa_E = \kappa_L + \sigma * L * T = \kappa_L + (L * T)/\rho, \tag{3}$$

where  $\kappa_L$  represents the lattice contribution in thermal conductivity ( $\kappa_L=0.5$  W/m.K, for unsubstituted tetrahedrite)[13,36] and L represents the Lorenz number, calculated through the formula L ( $10^{-8}V^2/K^2$ ) = 1.5+exp(-|S|/116). With this approximation, a zT=0,32 at 300K was achieved for Cu<sub>11,5</sub>Ni<sub>0.5</sub>Sb<sub>4</sub>S<sub>12.5</sub>Se<sub>0.5</sub>, which is a high figure of merit that must be taken into consideration with reservation, waiting for further results to be validate.



Fig. 10. Temperature denpendance of the electrical resistivity (A) and Seebeck coefficient (B) of Cu<sub>12-x</sub>Ni<sub>x</sub>Sb<sub>4</sub>S<sub>13-y</sub>Se<sub>y</sub> samples



Fig. 11. Temperature dependance of the electrical resistivity (A) and Seebeck coefficient (B) of  $Cu_{10,5}Ni_{1,5}Sb_4S_{13-y}Se_y$  samples compared with undoped tetrahedrite  $Cu_{12}Sb_4S_{13}$ 

Table 2. Electrical resistivity, Seebeck coefficient, PF, estimated thermal resistivity and figure of merit of  $Cu_{12-x}Ni_xSb_4S_{13-y}Se_y$  samples at 300K

X	Y	ρ (μ <b>Ω</b> m)	S (µV/K)	PF (µW/m.K <sup>2</sup> )	к (µW/m.K)	zT
0	0	24	59,5	147,51	0,76	0,06
0,5	0,5	8,4	103,6	1277,73	1,18	0,32
0,5	0,5	16	58,3	212,43	0,89	0,07
1	0,5	21,4	-	-	-	-
0,5	1	17,3	76,2	335,63	0,85	0,12
1	1	219,9	106,2	51,29	0,53	0,03
1,5	0	50,6	110,4	240,87	0,61	0,12
1,5	0,5	208,7	178,2	152,16	0,52	0,09
1,5	1	34,7	79	179,86	0,67	0,08
1	1,5	667,1	74,9	8,41	0,51	0,01
1,5	1,5	65,5	-	-	-	-

### CONCLUSIONS

The present work has shown that the tetrahedrites containing Ni and Se can be produced with only a casting step, although the presence of these dopants fosters the formation of secondary phases, particularly in high dopant content samples. It has also shown that an annealing step can greatly contribute to mitigating the formation of these phases, but it is not enough to fully suppress them in samples with high dopant content. Samples with these dopants are shown to be prone to porous formation and very brittle. The Ni-Se doped materials also maintain the highly degenerate semiconducting behaviour characteristic of tetrahedrite. The impact that these dopants had on the thermoelectric properties seem to indicate a potential improvement of the overall thermoelectric efficiency of tetrahedrite, even with just an annealing step. Particularly, the Cu<sub>11,5</sub>Ni<sub>0,5</sub>Sb<sub>4</sub>S<sub>12,5</sub>Se<sub>0,5</sub> sample shows a PF of 1277,73  $\mu$ W/m.K<sup>2</sup> at 300K, much higher than the previously described regarding tetrahedrites with these dopants ( $\approx 490 \mu$ W/m.K<sup>2</sup> at 300K). [13,17, 32, 34]

On the other hand, Cr doped samples have been shown to not readily integrate Cr within the tetrahedrite matrix and producing  $CuCrS_2$  needle-microstructures, which without chemical substitution of Cu for Cr in the tetrahedrite defeated the purpose of analysing the impact of double substitution on thermoelectric properties of these materials. Thus, the synthesis process for Cr doping needs to be reassessed, potentially by adding a sintering step.

It is important to mention that, despite existing numerous studies describing effects that chemical substitution with Ni, Cr and Se have in the thermoelectric properties of tetrahedrite, this simultaneous substitution with Ni and Se or Cr and Se have not been reported before. As mentioned before, there are plans to continue this research, which include the analysis of all annealed samples their sintering, which will hopefully mitigate the occurrence of other phases and the porosity of the materials, thus possibly providing better thermoelectric properties.

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# NATURALLY FRACTURED RESERVOIRS CHARACTERIZATION: BETWEEN ECONOMICALLY ATTRACTIVE AND OPERATIONALLY CHALLENGING

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#### ABSTRACT

Naturally fractured reservoirs (NFRs) are found worldwide, representing hydrocarbon reserves and other natural resources. In the past half-century, the petroleum industry has seen a growing awareness highlighting natural fractures' role in hydrocarbon recovery processes. Naturally fractured reservoir characterization is a complicated process. Not only matrix and fracture systems have to be studied, but also the interaction between the two continua must be analyzed accurately. Reservoir characterization in terms of geological and simulation modeling presents unique and specialized challenges that differentiate them from conventional, single porosity continuum reservoirs. Accurate, scientific, and scalable fractured reservoirs' characterization is paramount to capture the high contrasts in rock and fluid properties. Hence, efforts were devoted to quantifying fracture presence and its impact on the production mechanism. In this paper, various geological and engineering challenges associated with accurate modelling and characterization of naturally fractured reservoirs were identified and discussed. The main challenges are generally resulted from the reservoir heterogeneity, depositional processes, regional tectonic movements, high permeability pathways caused by the fractures, complicated and random distribution of fracture patterns, fracture geometry complexity, selecting the appropriate reservoir model, and lack of available fracture property details. A comprehensive understanding of these challenges enhances the modelling process and develops realistic reservoir models. This paper has also introduced a naturally fractured reservoirs classification based on the percent of total porosity and permeability. A methodology was presented to reduce the complexity and challenges associated with characterizing naturally fractured reservoirs.

**Keywords:** naturally fractured reservoirs; heterogeneity; challenges; reservoir characterization; reservoir classification; geological aspect

#### **INTRODUCTION**

A large amount of hydrocarbon reserves are trapped in naturally fractured reservoirs. These reservoirs are characterized by complicated structure and challenging fluid flow behaviour. Fig 1., illustrates a naturally fractured reservoir. NFRs are also considered as heterogeneous systems that consist of two porous mediums known as matrix and fracture. The rock matrix is generally responsible for a reservoir's storage capacity, while existing layer-bound and cross-layer fracture sets/corridors across a wide range of length scales define fracture connectivity characteristics [1] [2] [3]. The main objective of the paper is to raise the knowledge, awareness and challenges of naturally fractured reservoirs and highlight their roles in the production operations.



Fig. 1. Naturally fractured reservoir at Jebel Madmar in Oman

NFRs are considered as one of the most common and crucial geological structures in oil fields [4]. Due to the high heterogeneity of their porosities and permeabilities, modeling and characterizing natural fractures is becoming more and more difficult throughout the entire world for both old and new fields. Moreover, recent oil and gas field discoveries with natural fractures are considered to be unique both in terms of its geology and reservoir engineering issues, such as complication in Exploration and Production (E&P) operations [5]

The effect of vugs on permeability is directly related to the connectivity of these reservoirs. As fractures are with different scales, a reservoir's connectivity may range from poor to high, and the distribution may also be disorderly spatial [6, 7]. The presence of multi vugs will also improve secondary porosity. Thus, it is crucial to consider other advanced methods to characterize those reservoirs more efficiently than traditional conventional approaches. Most of the hydrocarbon volumes have not been produced because of several factors, including insufficient knowledge and less attention to dynamically model and characterize fracture systems in NFRs. The complexity of naturally fractured reservoirs requires a detailed dynamic model that integrates all existing information at all scales (drilling, well logging, seismic, well testing, etc.) to result in an accurate reservoir model that will provide the appropriate description for NFRs. Fig 2., indicates a complicated fracture network of a sedimentary carbonate outcrop



Fig. 2. Complex fracture network of a sedimentary carbonate outcrop

#### A GEOLOGICAL ASPECT OF NATURALLY FRACTURED RESERVOIRS

Fractured systems can be classified geologically, relying on the assumption that, at the fracturing time, natural fractures can be described by the paleo-stress conditions [8]. Fractures can be classified into three different types as follow: tectonic, regional, and contractional fractures. In tectonic fractures, the local tectonic events are the leading cause of fracture morphology, orientation, and distribution. This type of fracture occurs in networks and has a spatial relationship to faults and folds [9, 10]. The second type is known as the regional fracture system, which is characterized by long fracture sets and small orientation changes. These fractures' direction is often perpendicular to the bedding surface and exhibits no orientation across the fracture plane [11, 12]. The final type of fracture is known as contractional fractures; these fractures form as a consequence of the reduction in the bulk volume of the rock. Desiccation fracture might develop as a result of losing underground water and shrinkage in the subaerial formation. The process of cooling hot rock may result in thermal contraction. The complexity distribution of stress and strain values in subsurface formation leads to a complicated fracture pattern [13-15].

Fractured reservoirs often contain natural fractures that impact hydrocarbon movement in the subsurface formation, hence its modelling phase [16]. Massive amounts of the world's remaining oil and gas resources are contained within these reservoirs. Typically, their recoverable hydrocarbon is considered to be very low due to factors including poor swept efficiency and high residual oil. These factors are caused by high permeability pathways and significant matrix heterogeneity. The heterogeneity of fractures and matrix systems influences the productivity index and presents uncertainties during the modelling process. The distribution of fracture scale and size can vary significantly from one well to another across the reservoir. Generally, heterogeneities are sparsely sampled and poorly understood, leading to high uncertainty levels during the static and dynamic characterization process. Spooner, Geiger [17] and Wu, Cheng [18] have stated that NFRs comprise of fractures, vugs, and cavities. They all contribute largely to reserve oil and gas as well as providing effective paths for fluid flow.

Characterization of naturally fractured reservoirs has always been an attractive topic in early and current research [19]. Although such a system's primary porosity is limited, the production potential can still be high [20]. For example, in a karsted carbonate rock, the development and connectivity of cavities, including caves, caverns, or large-scale fractures, may enhance the system's fracture properties, i.e., porosity and permeability [21]. Usually, the fracture system helps to connect these karstic cavities [22]. Therefore, accurate modeling of karsted reservoirs could maximize oil and gas production and increase the recovery factor [23, 24].

According to Shen and Li [25], fractures are considered as an essential factor in controlling well performance in low permeability reservoirs. Naturally fractured reservoirs are highly heterogeneous, and their rock properties depend mainly on depositional processes. For example, tectonic events acting on the reservoir layers are believed to cause spatial heterogeneity in reservoir structures and mechanical properties. Studies have indicated that some geological factors, such as lithological features, porosity, structure, and thickness of the bed, can control the fracture intensity. Fractured reservoir characterization studies by Lorenz and Hill [26] have also illustrated that fracture systems might form in an irregular pattern usually disconnected and occurs in swarms. This makes the natural fractures in these reservoirs geologically challenging to detect and characterize. Besides, Aguilera [27] stated that most fractures occurring at depths below 760 m are nearly vertical or highly inclined fractures. Horizontal fractures at that depth tend to close due to the overburden pressure effects. He also

added that geologically, fracture generation is governed by three leading causes. Firstly, deformation in the earth's crust because of folding and faulting; this process is known as Diastrophism. Secondly, the upper part expansion and uplifting of the rock caused by deep erosion of the overburden, which leads to fractures formation through the plane's weakness. Finally, volume shrinkage occurs when the shale loses water to cool down the igneous rocks and desiccate sedimentary rocks.

Regional tectonic movements mainly cause formation microfractures to occur. Due to regional compression caused by overburden pressure, these fractures are mostly disconnected or even closed [28, 29]. Open microfractures have a significant impact on matrix properties leading to a better reservoir flow capacity. However, the industry still lacks the evaluation techniques to determine the micro-fractures effect on well productivity. It should be emphasized that it is economically attractive to produce NFRs, but it is also operationally challenging as, sometimes, predicting accurate fluid flow behavior is far from being attainable [30-33].

## CLASSIFICATIONS OF NATURALLY FRACTURED RESERVOIRS

Reservoir fractures might be associated with geoscience processes such as high stressdeformation, thermal loading in hydrocarbon formation, and tectonic forces. Geometric fractures in NFRs may vary both in size and scale. Furthermore, from a reservoir engineering aspect, the fracture system can be described in terms of permeability as highly, moderately, and poorly conductive. However, it should be emphasized that a fracture with poor conductivity may not necessarily lead to low matrix properties. For example, in most cases, micro-fractures are considered poorly conductive; in contrast, they may increase fractured reservoirs' matrix properties. The Overall storage capacity of microfractures might be greater than that of a formation matrix

The behaviour of naturally fractured reservoirs is difficult to predict and elusive to characterize. Therefore, it is essential to introduce basic criteria for recognizing these reservoirs' types, characteristics, and performance. The parameters may range from matrix dominated systems with some fracture enhancement to purely fracture dominated reservoirs. Nelson [20] classified naturally fractured reservoirs into four main types as follow:

### Type 1

In this type, fractures provide significant reservoir porosity and permeability. The drainage area of this type of reservoir is extensive. Several wells are required to be drilled for the field development phase. Type I reservoirs are characterized by very high initial rates that decline rapidly with production time. This type of fractured reservoirs is associated with difficulties in reserve determination as well as early water breakthrough.

## Type II

The overall conductivity of type II reservoirs is provided by fractures, whereas the rock matrix supplies the overall storativity. In type II reservoirs, the matrix has sufficient permeability to provide conductivity for fluid flow from the matrix to fractures. The initial rate for this type of reservoir can be high even in low matrix permeability conditions. When the communication between matrix and fractures is poor, type II reservoirs might be subjected to difficulties during secondary recovery mechanisms.

## **Type III**

Type III reservoirs are considered to be micro-porous and have moderate to high matrix porosity and low permeability. In this type of reservoir, both fractures and matrix systems govern the reservoir conductivity; however, the overall storage capacity is primarily dominated by the matrix system. Without fracture presence, most of type III reservoirs are incapable of producing at commercial rates.

## Type IV

Fractures in this type of reservoir are non-conductive due to the secondary mineralization processes occurring within the fracture. An example of these processes might be when seals and fractures are filled with minerals. Since the fractures' permeability is zero, the rock matrix provides the reservoir's overall conductivity and storativity.

Nelson [20] has introduced two types of fractured reservoirs in addition to the four main types stated above. These fractured reservoirs are known as type G and type M.

## Type G

This kind of reservoir is created particularly for unconventional fractured gas reservoirs and fractured gas condensate reservoirs such as Coalbed Methane (CBM). Most of type G reservoirs are located near or within the type II reservoirs.

## Type M

These reservoirs have decent matrix qualities, but they are sometimes compartmentalized. It may lead to production underperformance compared with early production estimates due to pressure issues. It will also make the secondary recovery effectiveness vary within the same reservoir. In type M reservoirs, the rock matrix supplies both the overall reservoir conductivity and storativity.

Generally, the reservoir quality is represented by the connectivity of reservoir formation and its permeability. Moreover, the rocks' petrophysical properties such as saturation exponent, grain density, porosity, and formation factor can identify the fractured reservoir's quality. In tight and heterogeneous reservoirs, fractures can enhance the connectivity of the pores by granting the well with connected fluid flow pathways through the fractured formation [34-43]. The dual permeability system with hydrocarbon flow through the fracture networks and matrix blocks is typically expected in naturally fractured reservoirs. The fracture system in such reservoirs may dominate the permeability and the direction of hydrocarbon flow [39]. In addition, natural fractures may intersect single or several beds, which remarkably affects the permeability magnitude in such reservoirs [44].

Natural fractures might impact both borehole instability and reservoir pressure. It increases the former and decreases the latter. After the production period, the fracture space may close partially or entirely [20]. Besides, reduction in the reservoir porosity and permeability may occur when non-hydrocarbon fluid passes through the fractures and dissolves in them, causing the deposition of secondary minerals in the fracture network [45, 46]. Therefore, to evaluate and optimize oil and gas production in fractured reservoir rocks, it is essential to understand the geological history of the fracture system as well as their diagenetic evolution [47]. Furthermore, understanding the influence of fractures on hydrocarbon flow and accurate prediction of fracture network distribution can positively enhance the reservoir quality

and reduce the modeling process's uncertainty and complexity. You, Wang [48] have added that fracture networks could potentially improve the transport volume of hydrocarbon in NFRs.

### **PROPOSED METHOD**

Naturally fractured reservoirs can be characterized using two main different sources; firstly, static data including seismic, well logs, core description, borehole images, tectonic history, geological structure, etc. Secondly dynamic data such as simulation study, well test data and wells production history. There are various reservoir simulation approaches to model naturally fractured reservoirs. Selecting the appropriate method should mainly depend on the type of the reservoir as well as on the primary objectives of reservoir simulation.

The first stage of naturally fractured reservoir simulation is developing a static model that provides a geological description of the natural fractures' origin and types. It will also set the factors controlling differences in fracture orientation and intensity over the whole reservoir. Static fracture model can be calibrated and constrained locally at the wellbore with image logs and core data. Static model is built to model attributes such as fracture intensity and orientation.

The following stage of the modelling process is to construct the dynamic model, this involves assigning hydraulic properties such as saturation functions, well control data, compressibility of fracture, etc. to the dynamic model. Hydraulic parameters can be derived from both well test interpretation and micro images log analysis. During this phase various parameters in different regions may indicate the presence of systematically variations in fracture networks (conductive properties). From a dynamic modelling aspect, in order to build a predictive reservoir simulation model, it is important to understand the high contrast in fluid flow behaviour in reservoir fractures.

A Hybrid Dual Porosity/Dual Permeability model with a superimposed computational grid is used to simulate the fractured reservoir. In this model matrix and fracture systems are considered as two separate continuous mediums. The use of dual-continuum model allows the flow between matrix gridlocks, which leads to more accurate simulation of NFRs. Moreover, this method also provides the ability to establish the matrix- fracture fluid interaction. Another important advantage of this model is that the matrix block connections takes into account the capillary continuity that has a vital implication on the gravity drainage recovery process for the fractured reservoir.

The modelling process is conducted based on unsteady state (USS) simulation in which fractures are expected to widen, lengthen, and close during the production phase. This means the fracture have a great effect on the hydrocarbon production. To appropriately describe these processes a permeability pseudo-tensor as a function of pressure, stress and density of fractures is introduced. The permeability pseudo-tensor model assists in distributing the permeability of the fracture in various directions with the well pattern which will enhance the production performance and minimize the water channelling in the fractured reservoir.

A black oil simulator is used in modelling naturally fractured reservoirs. This model has three different phases, which are water, oil and gas, it also has three components (water, oil and gas). The gas in black oil model is called free gas if it is in the gas phase, whereas it is known as solution gas when it is found in the oil phase. The thermodynamic behaviour of the hydrocarbon system in the reservoir can be represented by two main components, which are the stock tank oil and the separator gas. Black oil model can be used for all depletion cases when PVT data are generated properly. Therefore, PVT studies are the main source of data supply for this method.

Upscaling which is also known as homogenization is the process of substituting all the heterogeneous properties such as permeability, porosity, and fluid saturations represented of a fine-grid cells with an equivalent effective property value represented by coarse-grid model.

The main objective of upscaling is to create upsclaed parameters and functions that can be used in coarse-scale models to provide flow solution in similar agreement with the fine-scale model. In this case equivalent may refer to either volume or flux vice depending on property type to be upscaled. The upscaling process is essentially based on averaging static and dynamic characteristics of a fine-scale model. However, a more fundamental reason for upscaling is that input/output behaviour is in a dynamic order much lower than number of grid blocks in the model. Therefore, upscaling is proposed to optimally describe the input/output behaviour of a reservoir system. If upscaling is required in the simulation process a homogenization technique will be used. This technique has been successfully applied to a variety of problems such as twophase flow in layered and fractured medium. It has several advantages over the other conventional methods such as Representative Elementary Volume (REV). Homogenization approach does not apply intuitive closure equations and it shows the explicit dependency of the upscaled parameters. This technique is based on well-defined procedure and assumptions.

Once the dynamic model has been constructed, multiple runs should be conducted and results will be obtained after which the model will be validated by history matching some of important parameters. The main procedure for history matching comprises of simulating the reservoir model through a non-idealized rate history, next the good match quality is extracted by identifying the miss-matches between observed and calculated pressure and production rates. However, when the production rate is changed during well shut-in, a time-step is applied to retard the simulation. To reduce the time stepping effect, a monthly time-steps with averaged rate will be used.

The history matching method proposed is based on adjusting various parameters automatically which is known as Automatic History Matching. It can be defined as the construction of an initial reservoir model from geological model that undergoes some systematic processes such as objective function and minimization algorithm. Since the relationship between the production data and the fracture intensity is nonlinear, therefore in order to minimize the objective function a nonlinear optimization method is required. A reduction in the objective function, which is responsible for the mismatch between observed data and calculated response from the simulator will be done by automatically adjusting the relevant parameters

The history matching technique consists of two modules namely, inversion and flow simulation. The inversion module controls the automated history matching process. During the inversion process, Gauss-Newton algorithm is used to minimize the objective function, whereas the Levenberg- Marquardt algorithm is used to condition non-well matrices when necessary. During the matching process some common parameters might be set to be automatically changed. Such parameters as, pressure, production rate, water oil ratio, gas oil ratio and water gas ratio. More importantlyfracture permeability is calibrated with historical production rate rather than grid block effective permeability. This allows achieving a good modelling consistency in naturally fractured reservoir characterization. An integrated modeling of Naturally Fractured Reservoirs framework is summarized in Fig. 3.



Fig. 3. Integrated modeling of Naturally Fractured Reservoirs Framework

### NATURALLY FRACTURED RESERVOIRS CHARACTERIZATION CHALLENGES

NFRs simulation is considered to be extremely challenging due to many factors, including; the complexity of fracture geometry and lack of available fracture property details, which accounts for high uncertainty levels during the modeling and reserve estimation processes [49, 50]. Additionally, many fractured reservoirs consist of complex geological structures with variable conductivity ranges, which favorably affects the fluid flow patterns. Thus, characterizing fluid flow in the presence of these conductivity contrasts is of greatest importance [51]. Moreover, modeling NFRs may associate with many computational challenges. Such challenges may include (a) the large size of the heterogeneous domain requires a high-resolution simulation grid [52], (b) non-linear behavior due to strong coupling results (e.g., capillarity), which may affect the stability and lead to convergence issues, (c) conductivity contrasts accounts for more bounding limits to the system and (d) complexity introduced by geomechanical effects [53, 54]. These challenges demand introducing more advanced methods to characterize the NFRs behaviour with efficient and scalable models while maintaining the optimum accuracy to capture the physical phenomena in NFRs [55].

Belhaj, Qaddoura [56], and Curtis [57] stated that unconventional reservoirs (UCRs) such as naturally fractured reservoirs are those with complex petrophysical properties, distinguishable geological and geochemical characteristics, challenging well-completion and recovery mechanisms. Because different forces like viscous, capillary, inertia, convection, adsorption, and desorption influence fluid flow through fractured formations. The characterization of naturally fractured reservoirs is essential to address fluid flow behavior issues. At all scales, fractured reservoirs are regarded as intrinsically heterogenic and randomly distributed. Several research works [58-64] have argued that NFRs are considered the most difficult and challenging sort of reservoirs in terms of characterization and modeling. Their complex structure consists of two comparatively independent mediums, one known as a fracture and another as a matrix. Aabø, Dramsch [65] stated that fracture systems' subsurface characterization is always challenging and demanding as typically, the fracture data will be available in different scales, varying ages, and quality. Understanding the control of fracture orientations and distributions certainly provide accurate prediction scenarios of fluid flow in fractured reservoirs. In addition, due to the mechanical interactions between distinctive karst elements and fracture networks, karsted carbonate reservoir characterization and modelling present enormous challenges [19]. Furthermore, challenges and uncertainties will arise when modelling naturally fractured reservoirs that contain complex fracture networks. One of the challenges that might result from the continuum modelling process is the difficulties in scaling the fractured reservoir parameters, whether fractures are integrated as part of the porous medium or treated explicitly.

Selecting the appropriate model for NFRs characterization and modelling remains the main challenge of the process [66]. As hydrocarbon production might be impeded or improved by natural fracture, the technical challenge might be encountered because of the fractured reservoir's complex flow simulation processes. Still, a potential high reward is likely expected [67]. Moreover, constructing the flow model of a naturally occurring fractured reservoir is difficult and challenging. To accomplish the modelling process, it is vital to compromise between geological and dynamic requirements. Geologically, fractured and faulted rocks are considered the discontinuous surface where their volume is created under different stress conditions. Therefore, production recovery can be high when fractures act as conductive flow paths; otherwise, lower hydrocarbon is recovered when fractures act as barriers. It relies on fluid circulation following their genesis as well as the stress history.

According to Long, Remer [68], fracture network simulation in fractured media provides complex challenges that are not present in a standard porous medium. This concept might be explained by the connection of geometric properties and topological properties of fracture systems with the dynamic processes occurring in the domain. Because fractures contribute to strong discontinuities that are not well represented by averaged descriptions, a natural fracture network will strongly impact some natural processes, including fluid velocity leading to inaccurate description of the continuum modelling processes. Furthermore, due to some challenges such as mechanical or chemical fluid-solid interactions in fluid flow modelling, flow processes themselves may also affect the fracture networks' nature.

## CONCLUSION

Naturally fractured reservoirs can store vast accumulations of hydrocarbon within their naturally occurring fractures and heterogeneous microstructures. At the same time, these reservoirs present some of the most daunting challenges the energy industry is faced with. Their characterization and modelling are extraordinarily challenging and require advanced optimization technologies to efficiently enhance reservoir performance and maximize hydrocarbon recovery.

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## NANOSTRUCTURED GLASSY CARBON SILICON CARBIDE MATRIX COMPOSITE FOR SUPERCAPACITOR ELECTRODES

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#### ABSTRACT

In this work a method for synthesis of nanocarbon silicon carbide matrix composite electrodes with high surface area are present, as well as physical and electrochemical characteristics have been investigated. The composite is based on the SiC matrix, obtained by slip casting method from slurry consisting of silicon carbide raw powder distributed in an organic binder. After removal of the organic binder, the phenolic resin imposed in the SiC matrix was used as a source of carbon. High temperature vacuum pyrolysis was the final stage for the creation of composite material that managed to release carbon residue from phenolic resin. The amount of carbon in the composite material is determined by the quantity of phenolic resin, which embed into the initial porous silicon carbide matrix. Revealing the main parameters of the material: porosity, density, specific surface area and carbon content. Scanning Electron Microscopy and Raman spectroscopy was used for carbon structure investigation. Carbon residue material in the composite presents a nanostructured glassy carbon grid including nanoporous carbon and graphene like domains. Such nanostructured glassy carbon material covers the surface of silicon carbide grains. The mechanism of charge accumulation as well as measurements of the capacitance and power characteristics of the fabricated electrodes was made by using cyclic voltammetry and galvanostatic charge/discharge method. The obtained results showed that the manufactured electrodes could be successfully used for creation of supercapacitors based on them.

Keywords: SiC, nanostructured glassy carbon, matrix composite, supercapacitor

## **INTRODUCTION**

One of the developments in modern radio electronics has led to the emergence of an increasing number of portable and autonomous devices, as well as electric vehicles. Such products need more and more capacious electric energy storage devices: electrochemical batteries, fuel cells and supercapacitors. In this case, due to its parameters and properties, supercapacitors or ionistors favourably differ from their rivals. The main advantages of supercapacitors are: 1) high charge-discharge currents and low charging time (5 - 15 minutes); 2) a large number of charge/discharge cycles (20,000 or more); 3) long service life (more than 10 years); 4) minimal degradation of properties; 5) low dependence of characteristics from the ambient temperature and complete absence of heating during operation; 6) light of weight and high strength to mechanical stress. The main disadvantages of ionistors are low working voltage (up to 3 V) and high cost of materials and manufacturing, however, despite the disadvantages of the ionistors, they have a significant prospect of improvement for the subsequent replacement of traditional energy storage devices, especially for electrical vehicles [1, 2].

The main materials which are used as electrodes of supercapacitors are porous carbon materials with a high specific surface for accumulation of charge. Also these materials must have low specific resistance to ensure the necessary level of current for the electrical circuit. As carbon electrodes materials are used: activated carbon, carbon black, thermo-expanded graphite, nanoporous carbon, carbon nanotubes, carbon aerogel, graphene, and other similar materials. One of the most prospective material for the electrodes is graphene or graphene like films, which, although didn't have a record value of the specific surface (theoretical 2500 m<sup>2</sup>/g), but have low resistance (comparable to high-conductive metals: copper, aluminum etc.  $10^{-8}$  –

 $10^{-7} \Omega \cdot m$ ), which makes graphene the ideal candidate for electrodes of ionistors. However, it is known that graphene is 2D material, but for obtaining the maximum adsorbed electric charge, it is necessary to have a 3D material with high porosity. 2D graphene is obtained on specially prepared and polished surfaces of copper foil, monocrystalline silicon, oxidized monocrystalline silicon and monocrystalline silicon carbide by a CVD method that is as close as possible to industrial techniques. The manufacturing of 3D graphene is a large exotic and technologically complex process, which is reproducible mostly in research laboratories [3, 4]. An alternative for 2D graphene material can be nanostructured 3D glassy carbon, which is synthesized by pyrolysis of phenolic resin, has a high specific surface area and high electrical conductivity. [5].

The aim of this work is a developing of a technology for obtaining of ceramic matrix composite 3D material consist of nanostructured glassy carbon grid and SiC powders as a supporting template, which has high porosity, low specific resistance and a high specific surface area in terms of dry matter, followed by the use as supercapacitor electrodes.

#### **EXPERIMENTAL**

The developed technology for obtaining a 3D ceramic matrix composite consisting of silicon carbide and nanostructured glassy carbon grid was based on slip casting method and can be conditionally divided into several stages. At the first stage, an organic binder consisting of 70% of paraffin and 30% of bee wax is formed. Then a binder heated till 90 °C was filled with the fine-grained silicon carbide powder with an average grains size of 3 microns. After the long mixing, the liquid mixture is poured into a molding form, and placed on a vibration stand to remove air and solidification at room temperature. After cooling down, the solid workpiece is extracted from the molding form, and is characterized by the following geometric dimensions: diameter 100 mm, thickness 5 mm. At the second stage, the organic paraffin-containing binder is removing from the workpiece by heating in the special rigging filled with kaolin filler in furnace at air atmosphere and a temperature of 575 °C. On this stage, the initial silicon carbide matrix in the form of microporous template is fabricate. After the binder removal, the workpiece retains sufficient mechanical strength to carry out the next technological step. At the third stage, the workpiece is impregnated with phenol-formaldehyde resin in an autoclave under a pressure of 3.5 atm and a temperature of 45 °C for 5 hours. Phenol-formaldehyde resin is a future carbon source in the final composite material. After impregnation, the resin inside the porous SiC matrix is dried and polymerized at a temperature of 150 °C for 10 hours in the drying box. At the fourth stage, a two-phase pyrolysis of polymerized resin is carrying: firstly, pyrolysis in the nitrogen atmosphere at a temperature of 850 °C, and at the second phase in a vacuum oven with a temperature of 1200 °C, finalizing the formation of ceramic matrix composite material. Further from the received workpiece were cut out electrodes of the necessary shape, electrical contacts were made from chemically stable stainless steel wire and foil and a test electrochemical cell with paper separator was assembled, in which a 1 M solution of sodium sulfate Na<sub>2</sub>SO<sub>4</sub> was used as an electrolyte.

For the obtained ceramic matrix composite material, measurements of porosity, density and specific surface area were carried out as well as the mass percentage of carbon content was calculated. Studies of morphology were carried out by using scanning electron microscopy (SEM) Leo-1420 at acceleration voltage 20 kV. Research of the form and structure of carbon were carried out by a Raman scattering method at LOTIS TII MicroRaman spectrometer (Minsk, BSU) with spectral range (330-1100 nm), micropower (20 mW) 532 nm laser and spot size about 1 $\mu$ m. Specific surface of the composite material was carried out by using nitrogen gas adsorption BET analysis obtained by ASAP 2020 V3.04 H. Studies of electrochemical properties of electrodes made from the obtained composite material were carried out according to a two-electrode electrochemical cell with 1M water solution of sodium sulfate. The average weight of the electrodes was about 35 g per electrode at approximate geometric dimensions of  $7 \times 5 \times 0.5$  cm.

## **RESULTS AND DISCUSSIONS**

In Fig. 1 SEM images of the original porous silicon carbide matrix after removal of the organic binder (Fig. 1 a) and obtained after high temperature pyrolysis of composite material (Fig. 1 b) are shown. Based on the porosity measurements of the original SiC matrix, made by the Archimedes method and calculated by the corresponding SEM images, after the removal of the paraffin binder, the porosity of the sample was about 50%, and the porosity of the final C/SiC composite – 29%. The density of the total composite was 1.56 g/cm<sup>3</sup>, the amount of carbon by mass – 8.5%, measured specific surface of the composite material was about 1200 m<sup>2</sup> per gram of carbon. The size of C/SiC matrix composite micropores, obtained by SEM images, is  $1\pm0.5 \mu m$  and size of carbon nanopores, obtained by BET analysis is  $3\pm0.5 nm$ . Measured electrical resistivity of the material was  $1.4 \times 10^{-3} \Omega \cdot m$ .



Fig. 1. SEM images of the original porous silicon carbide matrix after removal of the organic binder (a) and of final C/SiC composite material after high-temperature vacuum pyrolysis (b).

The initial porous SiC matrix has a complex disordered structure, and the powder grains themselves have a polyhedral relief and a high roughness surface (Fig. 1 a). All particles are in close contact with each other at least three points, which provides mechanical strength after removing the organic binder. After the processes of impregnation and pyrolysis, the surfaces of grains are covered with carbon film, which is formed continuously on all surfaces of SiC crystals, creating a three-dimensional network of carbon layers. In Fig. 1 b the C/SiC composite material after vacuum pyrolysis is shown. As it clearly seen one of the crystal grains is covered with nanostructured carbon material and graphene like flakes, also clearly visible the unfilled pore of the SiC matrix. In general, carbon films and layers mostly repeat SiC powder grains and locate in close contact to them through all matrix volume.

In Fig. 2 Raman scattering spectra obtained by the LOTIS TII MicroRaman spectrometer (Minsk, BSU) is shown. On the spectra of the initial SiC ceramic matrix (Fig. 2 a) there are standard peaks (787 cm<sup>-1</sup> and 967 cm<sup>-1</sup>) belongs to vibrations of covalent Si–C bonds of the silicon carbide hexagonal 6H–SiC polytype, while any peaks belonging to any carbon form are absent. On the spectra of the C/SiC ceramic matrix composite (Fig. 2 b) in addition to the peaks belonging to the initial silicon carbide, there are peaks characterizing the carbon structure appears. Carbon peaks are noted by the well-known set D (1354 cm<sup>-1</sup>), G (1584 cm<sup>-1</sup>) and 2D (2705 cm<sup>-1</sup>) peaks corresponding to the vibrations states of C-C sp<sup>2</sup> hybridization of the bonds

of carbon atoms. The aspect ratio between G and 2D intensities (Fig. 2 b) is 0.71, what can be identifying close to graphene like flakes or films. On other parts of the sample spectra were fixed with the same arrangement of the main peaks, but with a different ratio between them (0.2 -0.5). This is due to the formation of other allotropic forms of carbon: nanoporous amorphous carbon and nanostructured graphite. In general, the material obtained after high-temperature pyrolysis can be characterized as three-dimensional nanostructured glassy carbon of complex shape [6].



Fig. 2. Raman scattering spectra of the original ceramic SiC matrix (a) and the final ceramic matrix composite C/SiC (b).

Thus, based on the analysis of electron-microscopy images and Raman scattering spectra, the resulting 3D matrix composite C/SiC material consists of a silicon carbide, which serves as a base or template and carbon material in the shape of nanostructured glassy carbon layers formed on the surface of SiC grains. Carbon material will subsequently perform the function of accumulation and retention of the electrical charge of the ionistor.

To determine the charge-discharge mechanism of the test supercapacitor, cyclic voltammograms were performed (Fig. 3 a), and for gravimetric capacity (F/g) calculation – current charge/discharge diagrams was obtained at a current of 64 mA (Fig. 3 b). During cyclic voltammograms measurements, the potential was limited till 1.3 V to eliminate the influence of incidental faradaic processes at the boundary of the electrode-electrolyte section. The shape of the obtained curves has the form of hysteresis without failures and lifts, which corresponds to the adsorption mechanism of charge transfer from ions of electrolyte to electrodes matched for supercapacitors from carbon nanomaterials.



Fig. 3. Cyclic voltammograms (a) and a charge/discharge diagram (b) of the test supercapacitor cell.

The use of electrolyte based on 1M solution of sodium sulfate allowed increasing the working voltage of the test cell till 1.3 V, which in turn ensured higher currents produced by the cell into an external electrical circuit. This resulted in a maximum current of more than 400 mA in a short cut mode. The maximum of the specific capacitance, calculated according to the gravimetric method described in [7], per gram of carbon in the composite material, was 72 F/g. The maximum energy density of the cell reached 4.2 Wh·kg<sup>-1</sup> and the power density – 336.3 W·kg<sup>-1</sup> was obtained. Showed results is comparable with references [5, 8, 9].

#### CONCLUSION

Thus, as a result of the work, a composite material based on a silicon carbide porous matrix and nanostructured carbon material has been done. During high-temperature pyrolysis of phenolic resin the nanostructured glassy carbon was synthesized. This carbon material has a complex shape including nanoporous amorphous carbon, nanostructured graphite and graphene like flakes on the surface of SiC grains creating a 3D carbon grid. In such matrix composite material silicon carbide stays like a microporous template and a nanostructured carbon – like an electric charge collector. The electrochemical studies showed a charge-discharge mechanism characterized for carbon materials based supercapacitors, and the gravimetric capacity calculated for the carbon mass of the composite was 72 F/g. The developed technology for obtaining composite material allows it to form supercapacitor electrodes of various shapes and sizes, and can be easily adapted for mass production in the future.

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# MECHANISM OF MOLECULAR OXYGEN REDUCTION OVER NITROGEN-DOPED GRAPHENE-LIKE MATERIALS: A QUANTUM CHEMICAL STUDY

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#### ABSTRACT

The paper presents the results of quantum chemical calculations by the method of density functional theory (DFT) of the main elementary stages of the oxygen reduction reaction (ORR) in an acid electrolyte using catalysts - nitrogen-doped graphene-like nanoclusters. As models of graphene-like clusters the molecules of coronene (Cor) and their nitrogen-containing analogue with the piperysine configuration of two nitrogen atoms (NN(1-4)Cor) were used. The energies of physisorption complexes of Corr•O<sub>2</sub> and NN(1-4)Cor•O<sub>2</sub> were -0.13 and -0.40 eV, respectively. The energy of chemisorption complex of NN(1-4)Cor•O•O was -2.12 eV. The energy of the lower unoccupied molecular orbital in NN(1-4)Cor•O•O the chemisorption complex is negative (-1.73 eV), therefore it leads to spontaneous attachment of first electron and first proton to the complex according to the four-electron ORR mechanism with forming a radical [NN(1-4)Cor•O•OH]• in doublet state. The energy of this stage was -4.30 eV. Similarly, the next three stages of the pair (electron + proton) addition were considered with the energy effects -3.70, -3.30 and -3.27 eV respectively. At the last stage of the four-electron ORR, a complex of NN(1-4)Cor and water molecules bound with a hydrogen bond was formed. The structure of formed NN(1-4)Cor molecule is similar to its initial structure. The performed quantum chemical calculations have shown that the catalytic activity of nitrogen-doped graphene in ORR can be explained due to two factors: the reduction of the band gap compared to that of pure graphene-like cluster and the activation of carbon atoms adjacent to nitrogen atoms. Negative values of the binding energy of four electrons and protons indicate the spontaneous flow of ORR over the nitrogen-containing cluster.

**Keywords:** Density functional theory (DFT), Oxygen reduction reaction (ORR), Nitrogen-doped nanoclusters, Graphene-like nanoclusters, Four-electron ORR

#### **INTRODUCTION**

Fuel cell technology [1], one of the technologies of energy conversion and storage, which can play a vital role in ridding humanity of hydrocarbon dependence. In the oxygen reduction reaction (ORR), which is the basis of this technology, electricity is directly generated when electrochemical reduction occurs of molecular oxygen and hydrogen oxidation, and water is formed as the only by-product, which indicates the environmental friendliness of this process. In this reaction, as a rule, catalysts based on platinum group metals (PGMs) are used, which direct it along four-electron routes ( $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$ ) [2]. The disadvantages of such catalysts include a small stock in nature of the corresponding metals, high cost and the effect of poisoning their surface [3, 4]. In the search for substitutes for catalysts based on PGMs, the attention of many researchers has been drawn to carbon materials in the form of clusters of small size. Their obvious advantages include low cost, availability of carbon, and high stability. In particular, this applies to carbon nanotubes [5] and cluster systems of graphene-like structure [6], as well as related materials that show good performance in the oxygen reduction reaction (ORR) in alkaline electrolyte by activating these systems with introduced heteroatoms [7, 8], such as nitrogen (N), phosphorus (P), boron (B), sulfur (S), selenium (Se), bismuth (Bi), and mixtures thereof [9 – 11] into their structure. Their efficiency has been confirmed both experimentally [5, 12] and substantiated by quantum chemical calculations [13], however, it is inferior to the activity of catalysts based on PGMs in the acid electrolyte [14]. In addition, it is extremely difficult to control the synthesis of graphene-like carbon structures doped with heteroatoms with given properties, structure and composition. The possibility of formation of active sites of carbon catalysts, which lead to the course of ORR by two-electron mechanisms with the formation of hydrogen peroxide ( $O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$ ) as an intermediate, should also be taken into account. This is due to the fact that the four-electron mechanism of ORR involves the presence of sufficiently active catalytic centers capable of activating the  $O_2$  molecule until the break of the O–O bond and the formation of the O–H bond [15].

The article considers the main elementary stages of ORR, which take place in an acidic environment with the participation of nitrogen-doped carbon catalyst (cathode) by four-electron mechanisms. The energy effects of all possible elementary stages (sequential attachment of electrons and protons to the oxygen molecule adsorbed on the carbon catalyst) were calculated, and the equilibrium structures of the starting structures, intermediate, and final products involved in ORR were founded.

## METHODS OF CALCULATIONS

All calculations were performed using the program US GAMESS [16] by the method of density functional theory (DFT) [17, 18] with exchange-correlation functional B3LYP [19, 20] in the basis set 6-31G (d, p) with the involvement of Grimme dispersion correction [21, 22].

Polyaromatic coronene molecule (Cor) and a molecule in which two of its carbon atoms of the central hexagon are replaced by two nitrogen atoms were chosen as a model of nanoparticles of graphene-like structure. The isomer, when two nitrogen atoms in the central hexagon of the Corr molecule located in para-position (for brevity, it will be denoted as NN(1-4)Cor) in comparison with the meta- and ortho-positions was the lowest in energy.

## **RESULTS AND DISCUSSION**

From the charge distribution in the molecules Cor and NN(1-4)Cor (Fig. 1), it is seen that in the first of them the charges on the carbon atoms of the CenH have small positive values, while in the nitrogen-containing molecule, the carbon atoms located between the atoms of nitrogen, carry a fairly significant positive charge (0.285 a.u).

It can be assumed that the carbon atoms of the CenH of the molecule NN(1-4)Cor are activated by neighbouring nitrogen atoms. The increase in the reactivity of the molecule NN(1-4)Cor in comparison with the molecule Cor can be evidenced by a small difference in the energies of the lower unoccupied molecular orbital (LUMO) and the higher occupied molecular orbital (HOMO), which for the first of them is 1.13, and for the second reaches 4.03 eV.

The capability of a molecule to chemically bind other molecules is determined by the structure of its LUMO: those for the considered molecules are presented in Fig. 2, which demonstrates that in the Corr molecule, the carbon atoms that do not contribute to the LUMO are in a parapositions, the distance between them being 2.851 Å, does not promote the chemical binding of the O<sub>2</sub> molecule. The equilibrium distance in the O<sub>2</sub> molecule in the approximation used in this work is 1.216 Å (experimental value is 1.235 Å [23]). In the NN(1-4)Cor molecule, two pair of adjacent carbon atoms of the CenH make no contribution to the structure of the LUMO (the distance between them is 1.403 Å), which creates favourable conditions for the chemical

binding of the  $O_2$  molecule. The consequence of this charge distribution and the structure of LUMO in Cor molecules and NN(1-4)Cor is that if for both molecules there is a van der Waals binding of the oxygen molecule (Fig. 3), which can be considered as physical adsorption, the chemical adsorption is realized only for the nitrogen-containing matrix.



Fig. 1. Charge distribution (a.u.) in molecules Corr and NN(1-4)Corr



Fig. 2. The structure of the lower unoccupied molecular orbital of molecules Cor and NN(1-4)Cor



Fig. 3. Structure of adsorption complexes formed during physical adsorption of O<sub>2</sub> molecule by Cor and NN(1-4)Cor molecules and corresponding binding energies

In the van der Waals complex Cor•O<sub>2</sub>, the O<sub>2</sub> molecule is located parallel to the plane of the Cor molecule at the distance of 2.806 Å from the latter. For the prereaction complex NN(1-4)Cor•O<sub>2</sub> in the singlet electron ground state, it is noticeably smaller and is 2.380 Å. In [24], the values for a similar model are 2.854 and 2.461 Å, and the binding energies are -0.13 and -0.31 eV, respectively.

The physical adsorption of the  $O_2$  molecule on the N-free or nitrogen-containing carbon matrix, the bond length in the  $O_2$  molecule increases to 1.227 and 1.284 Å, respectively (Fig. 3), which means activation of the latter in comparison with the isolated state.

After the transition from physical adsorption to chemisorption on the potential energy surface of the system «molecule  $NN(1-4)Cor + O_2$ » several stationary points are localized, which correspond to stable adsorption complexes of different structure. The structure with the coplanar arrangement of the C–C and O–O bonds were the lowest in energy, and the length of the latter is 1.473 Å (Fig. 4).



Fig. 4. The structure of the adsorption complex formed by chemical adsorption of the O<sub>2</sub> molecule by the molecule NN(1-4)Cor

Despite the fact that in the chemisorption complex  $NN(1-4)Cor \cdot O_2$ , the atoms of the  $O_2$ molecule are connected by chemical bonds with the carbon atoms on which a considerable positive charge in the molecule NN(1-4)Cor was concentrated (Fig. 1), the electron density is transferred from the molecule NN(1-4)Cor just to them, q(O) = -0.298 a.u. As a result of such transfer, the value of absolute negative charge on the nitrogen atoms decreases sharply, and the positive charge on the carbon atoms (involved in the formation of the adsorption complex) increases. The redistribution of electron density between O2 and NN(1-4)Cor molecules is due to the higher electronegativity of oxygen atoms compared to nitrogen atoms, which was noted nitrogen-doped number of studies on the properties of graphene in а [25, 26]. Thus, it can be argued that the  $O_2$  molecule in relation to the NN(1-4)Cor molecule exhibits oxidizing properties.

The binding energy of the O<sub>2</sub> molecule with the NN(1-4)Cor molecule, which, according to the accepted model, can be considered as the chemisorption energy, was -2.12 eV. This energy is the sum of three contributions: the deformation energy of the molecule NN(1-4)Cor (1.86 eV), the energy (1.51 eV), which is spent on extending the O–O bond from the equilibrium in the O<sub>2</sub> molecule to its value in the adsorption complex NN(1-4)Cor•O<sub>2</sub> (1.473 Å) and the binding energy itself. It should also be noted that in the chemisorption molecular complex NN(1-4)Cor•O<sub>2</sub>, the energy of LUMO is negative (-1.73 eV), which creates favourable conditions for the attachment of the first electron, according to the mechanism of four-electron molecular oxygen reduction.

Spontaneous addition of the first electron to the adsorption complex  $NN(1-4)Cor \cdot O_2$  leads to the formation of two stable intermediates  $[NN(1-4)Cor \cdot O \cdot O]^{-1}$ . In one of them, the O–O bond

only lengthens (R(O–O) = 1.475 Å), and in the other (which turn out to be 0.86 eV more stable, and the distance  $O \cdots O$  is 2.100 Å) – the O–O bond is ruptures (Fig. 5). The broke of the O–O bond connection determines the further ORR route. In this case, four-electron reductions to two water molecules are realized, and in the second case, two-electron reductions occur with the formation of a hydrogen peroxide molecule as an intermediate compound.



Fig. 5. The equilibrium structure of  $[NN(1-4)Cor \cdot O \cdot O]^{\cdot}$ , formed due to additions the first electron to the adsorption complex  $NN(1-4)Cor \cdot O_2$ , and charge distribution on atoms

Quite a significant difference between the vertical and adiabatic electron affinity for the complex NN(1-4)Cor•O<sub>2</sub> (1.34 and 0.37 eV) indicates a significant rearrangement of the spatial structure of the formed anion radical [NN(1-4)Cor•O•O]<sup>•-</sup> in comparison with the initial chemisorption complex NN(1-4)Cor•O<sub>2</sub>, which is reflected in the break of the O–O bond. The further activation of oxygen atoms in the anion radical [NN(1-4)Cor•O•O]<sup>•-</sup> is also evidenced by the length (1.363 Å) of their bonds with carbon atoms, which significantly exceeds the characteristic value of the carbonyl bond length in organic compounds (1.22 Å), as well as a significant concentration of negative charge on O atoms (-0.490 a.u.). The latter circumstance is an argument in favor of the possibility of spontaneous further attachment of proton to the anion radical [NN(1-4)Cor•O•O]<sup>•-</sup>.

For the protonated radical intermediate [NN(1-4)Cor•O•OH]<sup>•</sup> is characterized by further increase in the distance O···O (R(O···O) = 2,554 Å), the rupture of the C–N bond in the molecule NN(1-4)Cor and a fairly significant value of LUMO energy for both  $\alpha$ - and  $\beta$ -subsystems (-1.70 and -2.48 eV, respectively), which, as noted above, promotes the spontaneous attachment of the second electron.

When using any of the non-empirical quantum chemical methods in calculating the energy effect of proton or electron attachment to an arbitrary molecule, the energy of the latter is assumed to be zero. However, the calculation of the energy of the sequential attachment of an electron and a proton to the same molecule can be replaced, using Hess's law, by the calculation of the energy of the attachment of a hydrogen atom to the original system. In this case, the energy of sequential attachment of an electron and a proton to the molecular chemisorption complex  $NN(1-4)Corr \cdot O_2$ was calculated the difference between as the total energies of the protonated intermediate [NN(1-4)Cor•O•OH] and the NN(1-4)Cor•O<sub>2</sub> system. This energy was -4.3 eV.

After the electron addition to the radical  $[NN(1-4)Cor \cdot O \cdot OH]^{+}$ , several isomers  $[NN(1-4)Cor \cdot O \cdot OH]^{-}$  are formed, which differ slightly in energy. For the most stable of them (Fig. 6), a small difference takes place between the vertical and adiabatic electron affinity of the radical  $[NN(1-4)Cor \cdot O \cdot OH]^{+}$  (1.13 and 1.26 eV, respectively). This indicates insignificant differences in the spatial structure of the neutral radical and the anion formed from it  $[NN(1-4)Cor \cdot O \cdot OH]^{-}$ .



Fig. 6. The radical structure [NN(1-4)Cor•O•OH]<sup>•</sup> (*a*) and related isomer [NN(1-4)Cor•O•OH]<sup>-</sup> (*b*) formed after the electron addition and their total energies (a.u.)

Despite the fact that in the anion  $[NN(1-4)Cor \cdot O \cdot OH]^-$  the negative charge on the oxygen atom of the hydroxyl group (-0.518 a.u.) in absolute value slightly exceeds the negative charge on the carbonyl atom of the oxygen (-0.509 a.u.), the most energetically advantageous was the attachment of a proton (the second, according to the general mechanism) to the last of them with the formation of a neutral intermediate  $[NN(1-4)Cor \cdot OH \cdot OH]$  (see Fig. 7). The energy of its formation, calculated by the reaction  $[NN(1-4)Cor \cdot O \cdot OH]^{\bullet} + H^{\bullet} \rightarrow [NN(1-4)Cor \cdot OH \cdot OH]$ , was -3.7 eV. The negative value of the LUMO energy in the neutral intermediate  $[NN(1-4)Cor \cdot OH \cdot OH]$  (-1.58 eV) causes the spontaneous addition of an electron (the third, according to the general mechanism).





The vertical and adiabatic electron affinities of the intermediate  $[NN(1-4)Cor \cdot OH \cdot OH]$  are 0.22 and 0.36 eV, respectively, which suggests a possibility of spontaneous attachment of the next third electron with the formation of the anion radical  $[NN(1-4)Cor \cdot OH \cdot OH]^{+}$ . The distance between the oxygen atoms of the hydroxyl groups in this anion is 2.364 Å, on which the negative charge is concentrated, which is -0,520 a.u., thus determining the possible places of attachment of a proton (the third, according to the general mechanism). The energy of sequential addition of an electron and a proton to the intermediate  $[NN(1-4)Cor \cdot OH \cdot OH]$  with the formation of a neutral radical  $[NN(1-4)Cor \cdot OH \cdot OH_2]^{+}$  is equal to -3.30 eV.

The radical  $[NN(1-4)Cor \cdot OH \cdot OH_2]^{\bullet}$  is characterized by a significant rearrangement of the spatial structure in comparison with the intermediate  $[NN(1-4)Cor \cdot OH \cdot OH]$ , as a result, the CO–O bond is broken and the formation of a water molecule bound by a hydrogen bond to the

hydroxyl group of the surface. As in any radical, it has  $\alpha$ - and  $\beta$ -subsystems in which the energies of LUMO are -1.74 and -1.69 eV, respectively. Therefore, the electron (fourth, according to the general mechanism) spontaneously joins the radical [NN(1-4)Cor•OH•OH<sub>2</sub>] with the formation of the anion [NN(1-4)Cor•OH•OH<sub>2</sub>]<sup>-</sup>, in which the water molecule has a hydrogen bond with the hydroxyl group (Fig. 8).



Fig. 8. Equilibrium spatial structure of the anion [NN(1-4)Cor•OH•OH<sub>2</sub>]<sup>-</sup> with water molecule

Comparison of the radical  $[NN(1-4)Cor \bullet OH \bullet OH_2]^*$  and the anion  $[NN(1-4)Cor \bullet OH \bullet OH_2]^-$  shows almost the same spatial structure, which is a consequence of almost identical values of vertical and adiabatic electron affinities for electron radical  $[NN(1-4)Cor \bullet OH \bullet OH_2]^*$ , which are equal to 0.16 and 0.39 eV, respectively. In the anion  $[NN(1-4)Cor \bullet OH \bullet OH_2]^-$  the charge on the oxygen atom of the water molecule is -0.692, and on the oxygen atom of the hydroxyl group -0.528 a.u.

At the last stage of the four-electron ORR a proton joins the oxygen atom of the hydroxyl group of the anion  $[NN(1-4)Cor \cdot OH \cdot OH_2]$ , the CO–O bond is broken, and a complex is formed that remains almost unchanged in its structure NN(1-4)Cor, in comparison with the initial state, and a hydrogen-bound water dimer (Fig. 9). The energy of sequential addition of an electron and a proton to the intermediate  $[NN(1-4)Cor \cdot OH \cdot OH_2]$  with the formation of the final products was -3.27 eV.



Fig. 9. Structure of the final adsorption complex of oxygen molecule reduction on a nitrogen-containing carbon matrix

Fig. 10 shows the energies of all the stable structures formed from molecules NN(1-4)Cor and  $O_2$  during the four-electron routes of ORR. It shows that all intermediate stages of the reaction are exothermic, the energy effects of which naturally decrease in absolute value as the number of added electrons and protons increases. A significant decrease should also be noted in the system energy during the transition from physical adsorption to chemisorption.



Fig. 10. Energies of formation of the complexes realized during physical and chemical adsorption of O<sub>2</sub> molecule by NN(1-4)Cor molecule, as well as intermediates and complex of final products formed by sequential addition of four electrons and four protons to the adsorption complex NN(1-4)Cor•O<sub>2</sub> according to the four-electron routes of ORR. The sum

of the energies of the molecules NN(1-4)Cor and  $O_2$  is taken as the zero energy level

## CONCLUSIONS

Thus, from the analysis of the data obtained within the theory of functional density, several important conclusions can be drawn. The catalytic activity of nitrogen-doped graphene in the oxygen reduction reaction can be explained by a combination of several factors, namely the reduction of the band gap in nitrogen-containing clusters compared to the parent, purely carbon, cluster and the activation of carbon atoms by the neighbour nitrogen atoms. The calculation of the energy of the individual stages of addition of each of the four electrons and protons indicates a spontaneous course of the ORR on the nitrogen-containing cluster.

In the proposed consideration ORR one of the possible structures was used formed by doping the original pure carbon graphene matrix. With other mutual arrangements of nitrogen atoms, other types of activation of carbon atoms are possible, which are neighbours with N atoms embedded in the graphene matrix. Therefore, under real conditions it should be expected that ORR can occur simultaneously by four- or two-electron mechanisms of them, dependent on the microstructure of the active sites formed during the chemical production of nitrogen-doped samples of graphene.

To complete the description of ORR on nitrogen-doped graphene, it is also necessary to take into account the presence of defects of different nature, always present in the structure of graphene, which can significantly change the reaction path of molecular oxygen reduction.

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# MOLECULAR DYNAMICS SIMULATION OF THE LIQUID AL-CU ALLOYS

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#### ABSTRACT

Al-Cu alloys are important materials for vehicles and aircraft due high strength to density ratio. They are also explored for hydrogen related applications, such as hydrogen storage, due forming of Al<sub>2</sub>CuH compound. The knowledge of the structure and properties of the corresponding melts is necessary for an effective control of solid phase formation processes. The experimental X-ray diffraction study of binary melts Al40Cu60 (at 1,010 and 1,310 °C) and Al25Cu75 (at 1,100 and 1,400 °C) was performed. Molecular dynamics (MD) simulation of short-range order of Al<sub>86</sub>Cu<sub>14</sub>, Al<sub>75</sub>Cu<sub>25</sub>, Al<sub>70</sub>Cu<sub>30</sub>, Al<sub>60</sub>Cu<sub>40</sub>, Al40Cu60 and Al25Cu75 melts was also performed using several interatomic interaction potentials. Determination of the correctness of the used potentials was performed by comparing the structural factor (SF) and the self-diffusion coefficient of melts, calculated by MD methods, with experimental data. It was found that the bond-order potential (BOP) is the best choice for simulations. The BOP has a large potential cut-off, which is sufficient to describe medium range order in binary Al-Cu melts. In particular, a satisfactory coincidence between experimental SF and model SF at the low-angle region with diffraction vector value of up to 2 Å<sup>-1</sup> (pre-peak region) occurs when using BOP. It was found that the prepeak on total S(Q) for Al-Cu melts are caused by medium range order of Cu atoms. The intensive interactions in Al-Cu pairs have been also established. Presence both intensive heteroatomic interactions and MRO may result in the formation of structure of the Al<sub>2</sub>Cu intermetallic compound or icosahedral short-range order (ISRO) structure. The last one is characterized by the presence of a large number of tetrahedral, octahedral and icosahedral voids that is very promising for hydrogen related applications.

Keywords: aluminum-copper alloys, hydrogen storage, liquid state, molecular dynamics

#### **INTRODUCTION**

The Al–Cu alloys are important structural materials in the aerospace and power industries due to their high strength-to-density ratio and high electrical conductivity. The Al-Cu are also new materials for hydrogen-containing structures due to their potentially high resistance to mechanical degradation from hydrogen adsorption.

Diffraction research methods are direct methods for obtaining very important and reliable information about the local atomic structure in metallic melts and glasses. It should be noted that high-temperature X-ray diffraction experiment is very difficult to perform but it provides limited data about short-range order (SRO) in melts. Therefore simulation of the SRO of melts is usually carried out in parallel with experimental studies. Analysis of obtained structural models provides information on interatomic distances, coordination numbers, such as coordination polyhedra, orientational correlation in atom-atom-atom bonds. The obtained information can be compared with the data of solid-phase analysis in order to find structural elements that are formed in a liquid and are retained during crystallization. One of the most common methods for modelling metallic melts is the molecular dynamics (MD) method using calculated interatomic interaction potentials. The main problem of MD is the reliability and justification of the potentials [1] that are used for simulation of a Al-Cu melt structure.

For the first time, the paired long-range potential for Al-Cu system was obtained on the basis of the embedded atom method (EAM) [2]. Modelling Al-Cu alloys using the EAM pair potential is also considered in [3]. The modified embedded atom method (MEAM) is a result

of addition angular component to mentioned EAM potential. This method is a continuation of the formalism of the MEAM and the recently developed approximate second nearest neighbor method (2NN MEAM) [4]. To study alloying of metals in [5] the previous set of MEAM potentials for interactions between Al, Si, Mg, Cu and Fe atoms was optimized based on the combination of MEAM potentials of each element. The MEAM parameters of individual cells were optimized to better fit the generalized stacking fault energy (GSFE) curves compared to ab initio curves. The MEAM formalism allows one to combine any of these potentials to simulate the properties of multicomponent alloys.

An angular-dependent potential (ADP) have developed in [6]. It was based on the known potentials of the EAM for Al and Cu and parametric fitting of the cross-interaction functions in experimental and calculated data using the ab initio method. The obtained potential accurately and reliably reproduces the phase stability and  $\theta$ - $\theta$ ' phase transformation in the Al-Cu system, the enthalpy of mixing of alloys and other thermodynamic properties.

A high-precision analytical potential BOP (bond-order potential) for the Al-Cu system was developed in [7], the code of which is publicly available in the MD package LAMMPS [8]. The BOP provides a good description of the melting point, defect characteristics, and surface energies. Most importantly, this potential is capable of covering the Al-Cu phase diagram region enriched with Al. This potential is especially interesting because it is the study of the formation of the Al<sub>2</sub>Cu compound that is the prerequisite for the correct description of the hydrogen absorption by the obtained solid materials.

The structural dynamics of the  $Al_{80}Cu_{20}$  melt was studied in [9]. To study the evolution of the atomic structure of diffusion processes, viscosity, and brittleness, the ab initio method was used, which was compared with the method based on semiempirical potentials and with experimental data. An increase of the diffusion coefficient of a labeled Cu atom in the  $Al_{80}Cu_{20}$ melt was recorded as compared to the self-diffusion of a pure Cu melt. This conclusion is consistent with the results of the quasielastic neutron-scattering (QENS) method. The interdiffusion coefficients indicate the anomalous nature of the structural dynamics, in which local ordered clusters dominate in the  $Al_{80}Cu_{20}$  melt. The number of icosahedral clusters increases sharply when the liquid becomes more ordered with decreasing temperature, leading to the formation of icosahedral cavities. In addition, based on the Warren-Cowley close order parameter, it can be seen that Al and Cu atoms compete for the approach of Al atoms to their first coordination sphere as the temperature decreases. The deformation electron density shows that the intrinsic tetrahedral bonds in face-centered clusters (FCC) Al and Cu are transformed into the amorphous type in liquid  $Al_{80}Cu_{20}$ .

*Ab initio* MD simulation of the Al<sub>100-x</sub>Cu<sub>x</sub> melt, where x = 30 and 40, in a stable and supercooled state was carried out to study the correlation between structural (structural factors and pair correlation functions) and dynamic (self-diffusion coefficients, relaxation time and viscosity) depending on temperature properties [10]. The temperature evolution of diffusion, relaxation time and viscosity shows compliance with the Arrhenius law at high temperature and deviation from the law at low temperature, which occurs at the intersection temperature T<sub>X</sub> near the liquidus temperature (T<sub>X</sub> = 900 K for x = 30 and 1000 K for x = 40). The authors found that T<sub>X</sub> also corresponds to the appearance of dynamic inhomogeneities, which are formed in a supercooled state and exhibit features characteristic of this phenomenon. The total structural factors (S(Q)) show a prepeak, which becomes more pronounced with decreasing temperature and more significant for Al<sub>60</sub>Cu<sub>40</sub>, while partial S<sub>ij</sub>(Q) indicate that this prepeak is associated with Cu-Cu interactions. The analysis of pair correlation functions (g(r)) shows a shift of Cu atoms beyond the short-range order, even in favour of the development of the MRO based on Cu for both alloys upon cooling, and indicate the emergence of ISRO. It was also noted that the evolution of the ISRO correlates well with the change in viscosity. Finally, it was shown that the MRO is formed by linked fivefold bipyramids and their formation correlates with the appearance of dynamic heterogeneities.

The structural and transport properties of Al-Cu melts was investigated by ab initio molecular dynamics (AIMD) calculations [11]. A thin premium and a prepeak on the partial  $S_{ij}(Q)$  corresponding to the Al-Cu and Cu-Cu atomic pairs were discovered and confirmed by the experimental data in [12]. A strong heteroatomic interaction has been identified. Atomic clusters of the icosahedral type are the most common structures found in the Al<sub>80</sub>Cu<sub>20</sub> melt, the content of which decreases with increasing temperature. At the same time, MD modelling based on the potential of MEAM and AIMD [9] did not give similar results. The study of the liquid alloy Al<sub>80</sub>Cu<sub>20</sub> shows the importance of the formation of complex atomic structures leading to the growth of a close-packed structure with decreasing temperature.

An coincidence of the experimental self-diffusion coefficient of Cu with the presented MEAM-MD models was found. At the same time, a significantly lower coefficient of interdiffusion is observed in comparison with the experiment in the liquid alloy  $Al_{80}Cu_{20}$ . The viscosity was modelled using two MD methods and showed little deviation from experimental data. Satisfactory agreement between the MEAM-MD simulation and the experimental structural data of the  $Al_{83}Cu_{17}$  melt can also be noted.

The structural data of Al-Cu binary melts (from hypoeutectic  $Al_{93}Cu_7$  to hypereutectic  $Al_{70}Cu_{30}$ ) obtained by X-ray diffraction and AIMD method are presented in [13]. An excellent coincidence of experimental and simulated S(Q) was noted for all investigated melts. The diffuse properties of Al and Cu demonstrate a strong deviation from the Arrhenius law with a change in the Cu concentration from 7 to 30 at.%. This behaviour correlates with a change in the local ordering in melts, which is numerically characterized by the coordination number, bond angle distribution, orientational bond order, and parameters of Voronoi tessellation analysis. The microstructure of liquid Al-Cu alloys tends to form a crystal-like local atomic ordering of  $Al_2Cu$  during cooling, especially in hypereutectic melts.

As conclusion, in literature it was experimentally investigated and *ab initio* modelled only Al-rich Al-Cu melts, and only it is one article [26] where classical potentials was compared. In our work, we firstly obtained a X-ray diffraction curves for Cu-rich Al-Cu melts and used new BOP potential for investigation of it. We obtained a experimental structure factor and pair correlation function for liquid Al<sub>40</sub>Cu<sub>60</sub> and Al<sub>25</sub>Cu<sub>75</sub> at the temperatures +50 °C and +350 °C above liqudus line. Also we made a comparison of all available in LAMMPS classical potentials for investigation of Al-Cu melts.

#### METHODOLOGY

The binary Al<sub>40</sub>Cu<sub>60</sub> and Al<sub>25</sub>Cu<sub>75</sub> samples (all concentrations are given in at. %) were prepared by arc-melting the high purity Al (99.99 wt.%) or Cu (99.8 wt. %) in a water-cooled copper crucible under argon atmosphere. The samples were prepared placed in an alumina crucible and the special resistant heater inserted into the high-temperature chamber was used for progressive heating up to experimental temperature in helium atmosphere. The X-ray diffraction measurements for the liquid Al<sub>40</sub>Cu<sub>60</sub> (at 1,010 and 1,310 °C) and Al<sub>25</sub>Cu<sub>75</sub> (at 1,100 and 1,400 °C) alloys were carried out by means of  $\theta$ - $\theta$  diffractometer. The Zr–Y differential filters were used for monochromatization of Mo $K_{\alpha}$ -radiation ( $\lambda = 0.71069$  Å) diffracted from the surface of melts. The magnitude of experimental diffraction vector ( $Q = 4\pi \sin \theta / \lambda$ , where  $\theta$  is the half of the scattering angle) was ranged from 0.9 to 12.5 Å<sup>-1</sup>. Three sets of diffraction data were collected for each of the liquid alloy in order to minimize random errors.

The scattered X-ray intensities were corrected for the effects of air-scattering, absorption, polarization and Compton scattering [14] and converted to electron units per atom  $I^{\text{coh}}(Q)$  by

the generalised Krogh–Moe–Norman method [15, 16]. The total structure factor (S(Q)) was derived from  $I^{\text{coh}}(Q)$  by the relation [17]:

$$S(Q) = \frac{I^{coh}(Q)}{N \sum c_i f_i^2},$$
(1)

where  $I^{\text{coh}}(Q)$  - intensity of coherent scattering,  $c_i$  and  $f_i$  are the concentration and the atomic scattering factor for *i*-type atom, respectively [18]. The pair correlation function g(r) was obtained by Fourier transform of S(Q) using the equation

$$g(r) = 1 + \frac{1}{2\pi^2 r \rho \left(\sum_{i} c_i K_i\right)^2} \int_{0}^{Q_{\text{max}}} Q[S(Q) - 1] \sin(Qr) dQ, \qquad (2)$$

where  $\rho$  is the experimental density of liquid alloy,  $K_i^2 = f_i^2 / \sum c_i f_i^2$  averaged over scattering angles.

All MD simulation was performed by means of LAMMPS software package [8]. For each MD simulations of the Al-Cu melts starting cubic cell with periodic boundary conditions contained  $10^4$  randomly arranged atoms with corresponding composition. MD simulations have four main stages: 1) heating of initial configuration to 2,000 °C for melting and fast equilibrating by NPT ensemble; 2) cooling to temperature of x-ray diffraction study 3) annealing at this temperature until reaching an equilibrium state; 4) annealing of atomic configuration to equilibrium state by NVT ensemble. The sizes of cells were adjusted to the experimental atomic number density ( $\rho$ ) of alloys [19] at the temperatures of x-ray diffraction study. Timestep of MD simulation was equal to 0.3 fs and 100,000 steps was performed in each stage. The steps 3 and 4 have been repeated until obtaining a zero slope (within confidence interval) on energy vs timestep curve.

We used a final atomic coordinates after all steps and calculated model g(r) by averaging interatomic distances per atom. Then, we calculate model structure factor by means of reversed Fourier transform by mean of software, which developed in our laboratory, and compare it with experimental data.

A model self-diffusion coefficient is obtained as a slope of plot of mean-squared displacement (automatically calculated by LAMMPS) for each atom type vs time of modeling, which divided by 6.

#### **RESULTS AND DISCUSSIONS**

The main goal of this work is structure investigation of Al-Cu melts in wide concentration range (including a pure metal's melts) by mean of molecular dynamics method. For those we took and compared 7 ready potentials for LAMMPS from literature. For perfect filling of all concentration range, we additionally obtained a new X-ray diffraction curves for  $Al_{40}Cu_{60}$  and  $Al_{25}Cu_{75}$  melts at the temperatures +50 °C and +350 °C above liqudus line. Further, we investigated structure features as partial structure factors and pair correlation functions, prepeak presence and its origin, and connection between structure motifs, which saved in crystalline state.

The experimental total structure factors S(Q) and corresponding pair-correlation functions g(r) for liquid Al<sub>40</sub>Cu<sub>60</sub> and Al<sub>25</sub>Cu<sub>75</sub> at several temperatures are shown in Fig.1. The height of the first peak in the S(Q) and g(r) curves is decreased and the nearest neighbour distances (position of the first peak on g(r)) in the investigated liquid Al-Cu alloys are slightly increased with increasing temperature. The  $r_1$  and  $Q_1$  values determined as the position of the first peak of the S(Q) and g(r) are shown in Table 1 in comparison with experimental data for Al-Cu melts obtained in [20].



Fig 1. Experimental structure factors (a) and pair-correlation functions g(r) (b) of some alloys.

χ <sub>Cu</sub> , at.%	T, ℃ ± 5	$Q_{l}, \text{\AA}^{-1}\pm 0.01$	$r_1, \text{ Å} \pm 0.02$	Ref.
0	700	2.68	2.78	[20]
14	670	2.81	2.67	
25	670	2.89	2.60	
30	710	2.91	2.60	
40	810	2.93	2.56	
60	1,010	2.98	2.54	Present
	1,310	2.98	2.56	work
75	1,100	3.00	2.49	
	1,400	2.99	2.53	
100	1,220	3.0	2.46	[20]

**Table 1**. The experimental structural parameters of the liquid Al-Cu alloys.

For the Al-Cu system (Fig. 2), molecular dynamics modelling of the melt structure was carried out at a temperature 50°C above the liquidus line for Al<sub>100-x</sub>Cu<sub>x</sub> (x = 14, 25, 30, 40, 60, 75) melts and pure liquid Al and Cu, using different pair potentials: 4 EAM potentials and one of the potentials MEAM, ADP and BOP [2-7, 21; 22]. The verification of the correctness of the selected potential was controlled by comparing the calculated S(Q) with the obtained experimental total structure factors S(Q) and data taken from [20]. It may be noted that for all cases simulated S(Q) fit experimental data well in almost the entire range of diffraction vector. However, firstly the BOP provides the best description of the prepeak region (Q is up to 2 Å<sup>-1</sup>). Prepeaks in the structure factors of metallic melts at small Q-values are generally attributed to the medium-range order. In contrast to the EAM and ADP potentials, the cutoff in the BOP potential occurs at 12.6 Å that is sufficient to consider the MRO. The MEAM potential also allows us to simulate the MRO in melts, but a significant deviation of the prepeak intensity from the experimental values forced us to abandon it in favour of the BOP potential. Secondly, the BOP provides a good agreement of self-diffusion coefficients with data from *ab initio* calculation [10] (Table 2).

	Al (700 °C)	Al <sub>60</sub> Cu <sub>40</sub> (810 °C)		Al <sub>70</sub> Cu <sub>30</sub> (710 °C)		Cu (1120 °C)
Potentials	Al	Al	Cu	Al	Cu	Cu
ab initio [10]	0.61	0.34	0.31	0.36	0.33	0.32
EAM [3]	1.0561	0.5957	0.5331	0.5732	0.4918	0.4226
EAM [27]	0.6176	0.3365	0.2945	0.2446	0.2037	0.4545
ADP [6]	0.3183	0.0021	0.0016	0.0019	0.0009	0.355
MEAM [5]	0.00574	0.0438	0.0718	0.0010	0.0023	0.5238
BOP [7]	0.406	0.2199	0.2287	0.174	0.18	0.345
EAM [2]	0.8092	0.4275	0.4143	0.3787	0.3688	0.4437
EAM [22]	0.406	0.0898	0.0901	0.0542	0.0497	0.4463

**Table 2.** Comparison of self-diffusion coefficients of atoms calculated using variouspotentials ( $Å^2$ /ps) with the ones calculated in [10].

The accuracy of a certain of coefficient is determined by the last significant digit of the value.





The partial  $S_{ij}(Q)$  obtained from the MD models of the liquid Al-Cu alloys with high Al content are shown on Fig. 3. The partial structure factors  $S_{ij}(Q)$  points out that the pre-peak is

realized only in the  $S_{CuCu}(Q)$  curves. This fact is consistent with the results of *Ab initio* MD simulation [10] and RMC simulation [20]. It may be concluded that the prepeak on the total structure factor S(Q) is a result of the medium-range order of the MRO based on copper atoms. On the other hand, the deep minimum at small Q-values of the partial  $S_{AlCu}(Q)$  curves is a sign of a strong heteroatomic interactions in the Al-Cu melts.



Fig. 3. Partial structure factors for the Al<sub>70</sub>Cu<sub>30</sub> (a), Al<sub>75</sub>Cu<sub>25</sub> (b) and Al<sub>86</sub>Cu<sub>14</sub> (c) melts.





The corresponding partial pair correlations functions  $g_{ij}(R)$  are presented in Fig.4. The shortest interatomic distances are realized in Al-Cu and Cu-Cu pairs. However, high amplitude of the second peak in the  $g_{CuCu}(r)$  along with the high first peak on the  $g_{AlCu}(r)$  indicates that the Cu atoms have been also located in the second coordination sphere of a portion of the Cu atoms, thus suggesting a repulsion of Cu-Cu first neighbours. It was previously shown in [23] that the prepeak on the structure factor of liquid Al–TM alloys is caused by the chemical short-range order (CSRO). The repulsion of TM atoms from the first coordination sphere of TM to the second coordination sphere by Al atoms realized in the Al-based liquid alloys caused the reduction of the direct contact between transition metal atoms due to strong interaction in Al-TM pair.

According to the state diagram [24], the Al-Cu system contains the following phases:  $\theta$  phase (solid solution based on Al<sub>2</sub>Cu), solid solution based on aluminum (Al),  $\eta_1$  and low temperature  $\eta_2$  phases. Al<sub>2</sub>Cu crystallizes in a tetragonal lattice of its own type. The solid samples obtained after cooling of Al-Cu melts were investigated by X-ray phase analysis. It was found that main phase for the Al-rich samples is Al<sub>2</sub>Cu intermetallic compound (Fig.5). For example the Al<sub>75</sub>Cu<sub>25</sub> solid alloy contains Al<sub>2</sub>Cu phase and relatively small amount of Al phase, the Al<sub>70</sub>Cu<sub>30</sub> solid alloy contains only one phase – Al<sub>2</sub>Cu. This phase is very important for hydrogen-containing application due to ability of hydrogen absorption in the crystal lattice cavity, with the formation of Al<sub>2</sub>CuH<sub>x</sub> hydride [25].



Fig. 5. Diffraction pattern of the Al<sub>75</sub>Cu<sub>25</sub> (a) and Al<sub>70</sub>Cu<sub>30</sub> (b) solid alloys.

The crystal structure of Al<sub>2</sub>Cu phase is characterized by chemical short-range order: Cu atom has eight nearest Al neighbours in the solid state. On the other hand, the local structure in Al<sub>2</sub>Cu crystal phase are characterized by the following nearest interatomic distances:  $r_1$ (Al-Al) = 2.745,  $r_1$ (Al-Cu) = 2.585 nm,  $r_1$ (Cu-Cu) = 2.44 Å. Therefore, the both the CSRO and contacts between copper atoms, which are characteristic of the crystalline Al<sub>2</sub>Cu compound, are preserved in the Al-Cu melts. It may be noted that the CSRO in Al-based melts is usually connected with the formation of atomic clusters with an icosahedral short-range order (ISRO) [23].

### CONCLUSIONS

The X-ray diffraction studies of the  $Al_{40}Cu_{60}$  (at 1,010 and 1,310 °C),  $Al_{25}Cu_{75}$  (at 1,100 and 1,400 °C) melts and MD simulations of the  $Al_{86}Cu_{14}$ ,  $Al_{75}Cu_{25}$ ,  $Al_{70}Cu_{30}$ ,  $Al_{60}Cu_{40}$ ,  $Al_{40}Cu_{60}$  and  $Al_{25}Cu_{75}$  melts have been performed.

It was found that the MEAM, ADP and BOP methods are useful for studying the structure of binary Al-Cu melts. The corresponding potentials can describe interactions at a distance of at least 6 Å, that is sufficient for modelling the MRO in melts. It should also take into account that these potentials have an angular component, which plays a key role in the description of the solid phase formation. The best fitting of the experimental structure factor by MD results have been achieved using BOP.

It has been found that the Al-Cu melts with high Al content are characterized by presence of the CSRO and short interatomic distances in Al-Cu and Cu-Cu pairs. This feature may be attributed to the formation of an icosahedral short-range order (ISRO) or structure of the Al<sub>2</sub>Cu intermetallic compound. The ISRO is characterized by the presence of a large number of tetrahedral, octahedral and icosahedral voids, which can be filled later with hydrogen atoms. Therefore, it is promising to stabilize metastable phases with the ISRO by quenching the Al<sub>75</sub>Cu<sub>25</sub> melt. In the future, it is planned to perform Voronoi-Delaunay tesselation of the obtained MD models of the Al-Cu melts in order to investigate void distribution in atomic clusters.

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# SIMULATION OF CHARGED PARTICLE CHANNELING IN CRYSTALS

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#### ABSTRACT

Impurities and defects significantly influence properties of semiconductors, heterostructures, etc., thus the understanding of evolution processes of defects and impurities in these structures is necessary for their future development and improvements. For crystalline materials this evolution can be observed by Rutherford Backscattering Spectroscopy (RBS) and Particle Induced X-ray Emission (PIXE) techniques. The sensitivity of these techniques is increased when the impinging charged particles are parallel to the rows of atoms in the lattice and particle channelling occurs. As a result, particle flux is focused inside the channel and the interaction probability with the point defect or impurity located in the middle of the channel is greatly increased. In order to simulate channelling RBS and PIXE spectra, a validation of channelling model based on GEANT4 code was performed. Simulations of channelling have shown that incorrect energy loss of channelled particles was evaluated. Because of this, a modification was made to the model: instead of biasing the cross-sections of the physical processes, wrapper classes were used, which resized the interaction length for both discrete and continuous processes. The evaluated energy loss with the modification is in good agreement with the experimental values. Another modification of the current channelling model was made to include the critical angle for channelling. The simulated critical angle values are also in good agreement with the theoretical ones.

Further development of the model includes the modifications for better recreation of the experimental results, obtaining the theoretical RBS, PIXE and NRA spectra, and to obtain the theoretical distribution of heavy ions implanted in channelling directions. With the ability to correctly simulate the impurity and defect distribution RBS spectra, the model could be used for improvement of the properties of crystalline silicon used in solar panels.

Keywords: charged particle channelling, crystals

#### **INTRODUCTION**

The discovery of ion beam channelling as a phenomenon was made in the 1960-1965. When studying the ion penetration depth in aluminium, Davies and his co-workers observed not a Gaussian experimental ion distribution shape, but an asymmetric peak followed by an exponential tail [1]. The theoretical Gaussian shape was predicted with the assumption that the atoms in the solid are randomly located in space. The experimental observation could not be explained by this theoretical model. Later on, Robinson and Oen developed a theoretical computer model in which the atoms would be correctly assigned to their lattice sites [2]. While previously no account of the correlations between collision points were taken into consideration in the amorphous model, using the newly developed model it was observed that the 10 keV copper ions made very long flights along some of the crystal directions. These particles experienced many glancing collisions with the lattice atoms and thus were focused into the channels between lines of closely packed atoms. Thus, the experimental observation was proved to be due to ions travelling along the major crystal axis without experiencing large angle collisions. The observation was later experimentally proved by Piercy and co-workers when comparing ion penetration depth in amorphous and crystalline aluminium [3].

The extended range of the particle motion, small angle deflections, and focus of the particle beam inside the crystal channel allows for various applications, such as beam steering [4], splitting and focusing of external beam [5], beam collimation [6], enhancement of nuclear

reactions [7] and others. Of particular interest are studies of defect formation, annealing and evolution processes [8, 9]. As impurities and defects significantly influence the properties of semiconductors, heterostructures, etc, the understanding of the evolution processes of defects and impurities in these structures is necessary for their property development and improvements. Ion beam channelling can be used both for implantation of dopant atoms into crystalline materials and for the study of the peculiarities of implanted species incorporation into lattice, displacement damage, evolution due to temperature effects, etc. Main techniques used for latter are Rutherford Backscattering Spectroscopy (RBS), Particle Induced X-Ray Emission (PIXE) and Nuclear Reaction Analysis (NRA). Due to beam focusing in the channel, the impinging particle is more likely to interact with the impurity or defect located outside of the atom row (i.e., when the defect is in the middle of the channel) and thus the reaction can be observed. To obtain a better insight into channelling processes many simulation codes were developed, such as Marlowe [2], LAROSE [10], FLUX7 [11] and recently developed GEANT4 implementation [12]. Most of the simulation codes use either real atom positions for potential energy evaluation or uses atom string approximation for potential, developed by Lindhard [13]. Initial experimentation with GEANT4 [14] channelling code showed, that several key physical processes are not simulated correctly – notably the channelling critical angle limitation and energy loss evaluation. The aim of this work is to provide key modifications to the current GEANT4 based channelling model and provide the theoretical evaluation of channelling in silicon crystal based on ECHARM [15] and GEANT4 [14] codes. The model is being further developed to be able to simulate RBS spectra in channelling conditions.

#### METHODOLOGY

#### **Conditions of channelling**

The theoretical basis of the channelling phenomena was made by Lindhard [13]. The particle moving through a crystal experiences screened Coulomb interaction between the ion and the atoms. In such collisions, the particle must pass close to or through the atom. In the latter case, a large angle collision is observed and no correlation between collisions is expected. However, when the particle is close to the atom and small angle collision is expected, the deflections of the particle path are determined by the potential of the crystal lattice. Moreover, if the particle passes close to a single atom and only small angle deflection occurs, it must also pass close to the neighbouring atoms in the same row of atoms. Thus a correlation between successive collisions is expected. From this result, a simple concept of a string of atoms, characterized by the distance between neighbouring atoms can be made.

If the particle motion is governed by the number of correlated collisions with the atoms of the string, the motion can be approximated as if the particle moves under the influence of a continuum string potential obtained by averaging the potential in the axial direction:

$$U(r) = \int_{-d/2}^{d/2} V_c(\sqrt{z^2 + r^2}) dz, \qquad (1)$$

where  $V_c$  is the crystal potential, z is the distance travelled along the string, d is the distance between neighbour atoms, and r is the distance between the ion and string of atoms. By inserting the screened Coulomb potential, the axial continuum potential for static lattice is obtained:

$$U_{a}(r) = \frac{Z_{1}Z_{2}e^{2}}{d}\ln([Ca/r]^{2}+1), \qquad (2)$$

where  $C^2=3$ ,  $Z_1$  and  $Z_2$  are, correspondingly, particle and atom charge numbers, e is the elementary charge, r is the distance from the string, and a is the screening distance.

When small angle collisions are considered, the incident and exit angles of a channeled particle is conserved. This consideration gives the conservation of transverse (perpendicular to the axis of the crystal) energy:

$$E = \frac{p_x^2 + p_y^2}{2M} + U(r) = E\Phi^2 + U(r),$$
(3)

where U(r) is the crystal potential, M is the projectile mass and  $p_i$  is the momentum in the i<sup>th</sup> direction and  $\Phi$  is the angle of incidence. The critical angle for which the incident particle can be steered by the atomic rows is obtained when the critical transverse energy of the incident particle is equal to the transverse energy at the distance of the closest approach  $r_{min}$  (when the angle is equal to 0):

$$\psi_c = \sqrt{\frac{U(r_{min})}{E}}.$$
 (4)

The minimum distance  $r_{min}$  in static lattice is equal to the Thomas-Fermi screening radius of atomic interaction  $a_{TF}$ :

$$a_{TF} = 0.885 a_B \left( Z_1^{1/2} + Z_2^{1/2} \right)^{-2/3}, \tag{5}$$

here  $Z_1$  and  $Z_2$  are the charge numbers of projectile and target atom, respectively,  $a_B$  is the Bohr radius. Due to thermal smearing of the atom positions, a lower limit to the minimum distance  $r_{min}$  for which correlated collisions can occur is set. This limit is defined by the transverse root mean square thermal vibration amplitude  $\rho$ :

 $r_{min} \approx \sqrt{a_{TF}^2 + \rho^2}.$ 

By substituting the  $r_{min}$  in the potential equation (2) with (6) and combining equations (2) and (4), a critical angle for vibrating lattice is obtained:

$$\psi_{c}(\rho) = \frac{\psi_{1}}{\sqrt{2}} \left\{ ln \left( \left[ \frac{Ca}{r_{min}} \right]^{2} + 1 \right) \right\}^{\frac{1}{2}}, \tag{6}$$

where  $\psi_1$  is defined by:

$$\Psi_1 = \sqrt{\frac{2Z_1 Z_2 e^2}{Ed}}.$$
(7)

Equation (5) gives the critical angle of incidence for which the particle channelling can occur. This shows that due to increase in temperature, and, subsequently, increase in thermal vibrational amplitude, the maximum axial continuum potential and critical angle decreases. To sum up, the condition for channelling can be written as:

$$U_{\max} < E + U(r). \tag{8}$$

As long as the particle transverse and potential energy is lower than the maximum value of crystal potential (in the position of the atom), the particle can be steered inside the channel.

#### Evaluation of lattice characteristics with ECHARM code

The ECHARM calculation method relies on the classical physics equations and the Fourier expansion of periodic functions in a periodic structure (for more details see [15]). The steps of calculations are as follows - first of all, the fundamental properties of the atoms are defined: charge and mass numbers, Debye temperature, average ionization constant and form factor (Moliere or experimental). Then lattice is defined, either by choosing one of the predefined lattices (BCC, FCC, diamond, etc.) or by constructing the lattice from scratch (by defining the atom positions and angles of the primitive cell). After that, miller indices of the axis in which the particle channelling is to be calculated and two perpendicular planes are defined. Finally, the so called strip object is defined which combines the previously defined parameters to calculate the characteristics: average nuclei and electron densities, electric field

and crystal potential energy distributions perpendicular to crystal axis. In this work characteristics were evaluated for Si <001> and <110> axis with temperatures ranging from 100 K to 1400 K. Furthermore, two Debye temperatures were used for the simulations: 640 K (obtained from the heat capacity measurements [16]) and 490 K (obtained from the channeling experiments [17]). The mean squared thermal vibrational amplitude for specific temperature is obtained by [18]:

$$\langle A^2 \rangle = \frac{9h^2 T\left(\varphi(x) + \frac{x}{4}\right)}{4\pi^2 M k T_D^2},\tag{9}$$

here h – is Planck's constant, k is the Boltzmann constant, T is the investigated temperature, M – mean atomic mass,  $x = T_d/T$  is the ratio of Debye temperature to the investigated temperature, and  $\varphi(x)$  is the Debye integral:

$$\varphi(x) = \frac{1}{x} \int_0^x \frac{tdt}{e^t - 1}.$$
(10)

#### Simulation of channelling with GEANT4 code

GEANT4 is a widely used toolkit for the simulation of passage of particles through matter. Few of the advantages of the toolkit are that it is written in object-oriented C++ language, it is open-source, and new physical processes can be added to the provided standard ones. The channelling focused source code was first implemented in GEANT4 from the version 10.3 with the addition of crystalline structure class [12]. It was made for the simulation of channelling in straight and bent crystals with very high energy particles (400 GeV/c protons). The first version included the Crystal class by G4Extendedmaterial class for the description of a crystal structure, channelling process class and special *wrapper* classes to modify the cross section of existing physics processes according to density of nuclei and electron at each step of the particle motion. However, with the newest version (10.7) of the GEANT4, the wrapper classes are changed with the biasing operation classes. In principle, the newer classes should bias the cross section correctly as it was in the case of 10.3 version of channelling package. However, it was observed that the particle energy loss was exactly as if the material was amorphous, although the channelling conditions were clearly satisfied. Due to this incorrect evaluation of the energy loss, a modification was made to bring back the older wrapper classes, which were proved to produce expected results. The wrapper classes resize the interaction length of both the discrete and continuous processes by the average normalized density of electrons and nuclei based on the current particle position in the channel (obtained from ECHARM calculations). The stopping power of MeV energy ions in materials largely depend on local electron density along the particle path. Channelled particles tend to focus closer to the center of the channel, where electron density is low and energy loss is lower compared to amorphous case. On the contrary, when particles approach the atom strings (incidence angle close to critical one), where local electron density is high, the stopping power is increased. The local electron and nuclei densities are equal to 1 and independent of particle position for amorphous materials. On the other hand, these values can range by ~17 orders of magnitude in crystalline case (high probability where atom should be located and very low probability between two neighbouring strings of atoms). However, the average value of this distribution is still equal to 1.

Another additional modification of the code was made regarding the channelling condition. Preliminary simulations have shown, that critical angle is not accounted for in the current version of the channelling package. The modification was made according to equation (9): when the particle enters the sample, geometry is checked for whether the sample is crystalline or amorphous. If the sample contains the lattice, impinging particle position is

randomly generated in the perpendicular to the axis plane. At the next step of the particle, the condition is checked again. If the transverse energy is less than crystal potential maximum, the channelling can occur. However, if the transverse energy is bigger than the maximum potential, a dechanneling event occurs. At the succeeding step the condition is checked once again: this time if the transverse energy is lesser than the potential maximum, a random position is once again generated. By including such condition it is possible for the particle to dechannel and after some of the interaction steps, if the channelling condition is satisfied, the particle is once again treated as if it is in channelling geometry and rechannelling occurs.

#### Sequence of simulations

The evaluations presented here are performed by using ECHARM and GEANT4 codes. The simplified scheme of work sequence is presented in Fig. 1. The calculations are firstly made in ECHARM and the output characteristics (lattice constants, atom and electron densities, potential energy, and electrical field perpendicular to the crystal axis) are used in GEANT4 calculations. To compare results, some of the obtained parameters were evaluated with the widely used and validated Monte Carlo based channelling code FLUX7 [11]. The main feature of the code is that it uses discrete binary collisions instead of a continuum string approximation, and, in theory, should provide more accurate results. A brief description of the code can be found at [19].



Fig. 1. Scheme of work sequence

## RESULTS

Before channelling simulations can be performed in GEANT4, data files of crystal characteristics (see Fig. 1, orange arrows) must be prepared. This was done by using ECHARM. A diamond-type silicon lattice was used in simulations (lattice constant a = 5.431 Å). The width of a single channel (distance between strings of atoms) for <001> axis is about 2.716 Å. In order to investigate the influence of temperature on the channelling efficiency, average thermal vibrational amplitudes were evaluated. We define the ratio of the mean vibrational amplitude to the width of the channel as *R* for simplification reasons. At the temperature of 100 K, the mean amplitudes of atom vibrations is A=0.048 Å (R = 1.8 %) and A=0.058 Å (R = 2.1 %) for Debye temperatures of 640 K and 490 K, respectively (see fig. 2). In 1400 K temperature region, the amplitudes are A=0.133 Å (R = 4.9 %) and A=0.174 Å (R = 6.4 %), respectively. The difference between values obtained with different Debye temperatures ranges from 18 % in 100 K region to 27 % in 1400 K region. The increase of difference is due to the fact that the thermal vibrational amplitude depends on the temperature non-linearly, the reason for increase is the integral part in equation (10). The mean vibrational amplitudes increase around 2.75 times for  $T_d = 640$  K and 3.01 times for  $T_d = 490$  K when compared 100 K with 1400 K vibrational

amplitudes. The obtained results coincide well with the values obtained by other authors (see fig. 2).



Fig. 2. Thermal vibrational amplitude dependency on the temperature of the sample. Two curves obtained in this research and three curves from other authors are shown (digitized from [20]), corresponding to different Debye temperatures

The influence on potential energy distribution of these vibrations for Debye temperature of 640 K is shown in Fig. 3. As can be seen, the increase of sample temperature from 100 K to 1000 K decreases the maximum potential energy from around 106 eV to around 57 eV. The mean thermal vibration amplitude is A=0.113 Å (R = 4.2 %) at 1000 K. The same potentials were also evaluated for a Debye temperature of 490 K (see Fig. 4). In this case, the maximum potential value decreases from 95 eV at 1000 K to around 44 eV at 1000 K and the mean thermal vibration amplitude is A=0.147 Å (R = 5.4 %) at 1000 K. As noted in the section 2.1, the increase of mean thermal vibrational amplitude limits the closest approach distance (equation (6)) and due to this increased distance the maximum axial continuum potential decreases based on equation (2).



Fig. 3. Potential energy perpendicular to <001> axis of Si in two different temperatures: (a) 100 K, and (b) 1000 K. The Debye temperature used in calculations is 640 K



Fig. 4. Potential perpendicular to <001> axis of Si in two different temperatures: (a) 100 K, and (b) 1000 K. The Debye temperature used in calculations is 490 K

The critical angle evaluations for 1 MeV protons transmitted in parallel to the <001> axis of 10 µm silicon sample are presented in Fig. 5 (a) for temperature of 100 K and (b) for temperature of 1400 K. The critical angle  $\psi_1$  (obtained with equation (8)) is around 0.49°, while the critical angles according to thermal vibrations (obtained with equation (7)) are  $\psi_c = 0.66^\circ$  for 100 K and  $\psi_c = 0.46^\circ$  for 1400 K. As can be seen, the channelled proton energy maxima are around 0.89 MeV which is also the value obtained by FLUX7 calculations. The transmitted energy spectra show that when the theoretical critical angle is overcome, the energy distribution of transmitted protons approaches the amorphous case. Thus, a good agreement with theoretical expectation is achieved. Moreover, when the incident angle is close to critical angle, two important results are observed. The first one is that the higher than amorphous energy tail is observed – a fraction of particles are still channelled in the sample (although to lower extent). The other observation is on the opposite side of the energy spectrum. As can be seen in fig. 5 (d), there is a small fraction of particles that have lower energy than in the case of amorphous sample. This is due to the fact that the particles which approach atom strings with lesser distance interact with higher local electron density. Therefore higher energy loss is expected when compared to amorphous case (in amorphous case, electron and nuclei density are equal to 1). Thus particles, which are travelling closer to atom strings will have stopping powers even higher than in the random RBS case (incident angle far from any crystalline axis or planes) [21]. This phenomenon is experimentally observed when RBS yield dependence on the angle of incidence is evaluated [22]. We compared the number of transmitted protons that have energy less than 0.5 MeV between channelling at critical angle and amorphous cases. The results show that number of transmitted protons is higher by 15% (for 100K) and 25% (for 1400K) when compared to amorphous case.



Fig. 5. Energy of transmitted protons through 10 μm of Si along <001> axis at different sample rotatons: (a) 100 K; (b) 1400 K, (c) ratio of transmitted particles in 100 K to 1400 K; (d) low energy region at critical angle. The impinging beam energy is 1 MeV. Critical angles are shown in the plots. 50000 protons were simulated in each case

Another remark can be made regarding the number of transmitted particles at 100 K and 1400 K temperatures. Due to higher potential values for lower temperatures, not only the critical angle is higher, but the number of channelled particles is higher too (see Fig. 5, c). In the case of 0° incidence, the number of particles in the energy region of 0.85-0.9 MeV simulated in 100 K is by 50 % higher when compared to 1400 K case. As the angle of incidence increase, this difference drastically increases and can reach up to 18 times (0.4° incidence). Thus, crystal potential is higher and better channelling efficiency is observed at lower temperatures.

The comparison of transmitted energy spectra obtained from simulations and experiments in channelling and amorphous conditions is presented in Fig. 6. In this case 9 MeV protons were transmitted through 48  $\mu$ m silicon crystal parallel to the <110> axis. In case of random orientation (amorphous case), simulations were performed with GEANT4 and SRIM-2013 [23]. SRIM is a widely used, industry standard code for evaluation of particle energy loss, projected range, etc.



Fig. 6. Normalized to maxima energy spectra of 9 MeV protons transmitted in parallel to the <110> axis and in random directions of a 48 μm of silicon crystal. Experimental results were digitized from [25], theoretical distributions were calculated by GEANT4, FLUX7 and SRIM-2013. Simulations were performed with 50 000 particles in each case

Although both GEANT4 and SRIM curves coincide well with one another, but experimental distribution is wider and peak value is shifted by ~20 keV to high energy side compared to the simulated curves. This discrepancy may be attributed to two main reasons: fluctuations of experimental conditions (beam energy stability, detector energy resolution, etc.) and the existence of channelling to smaller extent. The second reason is more plausible due to sample being not amorphous. In crystalline silicone there is a high number of secondary axes. These axes could capture the impinging particle, and a lower energy loss when compared to amorphous case would be observed (for other channels in silicon see [24]). In case of channelling, the energy distributions of protons obtained by GEANT4 and FLUX7 simulations are in good agreement. However, the simulated particle energy is higher than the experimental data. This is mostly due to the fact, that the silicon lattice is assumed to be perfect in the simulations, while the experimental lattice almost always has defects (both at the sample surface and in bulk). Therefore, the channelling efficiency is worse and the energy loss is relatively higher.

### CONCLUSIONS

Preliminary numerical simulations with the original channelling code supplied with GEANT4 10.7 have shown that current code is not able to accurately simulate specific experimental results. These include the lack of evaluation of critical angle condition and incorrect energy loss for channelled particles. With the modifications provided in this paper, the critical angles obtained in simulations are in good agreement with the theoretical ones. Moreover, the GEANT4 simulated energy loss for protons is in good agreement with the values obtained by FLUX7 code. The difference between simulations and the experimental data are mostly due to the defects in the lattice. With the increase of angle of incidence, the proton energy distribution approaches the amorphous energy distribution. The comparison of energy distributions of 1 MeV protons transmitted through 10  $\mu$ m of silicon parallel to <100> axis shows that around 50 % more particles have higher energy when channelled at 100K than at

1400K temperature. This difference increase up to 17 times when 0.4° incident angle is used. When comparing cases of lattice temperatures of 100K and 1000K, the maximum crystal potential energy decreases by about 2 times. Thus, with increasing temperature, the maximum crystal potential energy decreases and this induces decrease not only for the critical angle, but also for the channelling efficiency.

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## ELECTRODEPOSITION OF NICKEL ON A MAGNESIUM SUBSTRATE

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#### ABSTRACT

Being extremely light, affordable, with good strength and non-environmentally harmful, magnesium has acquired over the last decades an increasing interest and an improved range of applications. Magnesium is one of the most commonly found elements on the earth's crust that, together with the above-mentioned properties, makes it widely used in the automotive and space industries, construction, and more recently in the biomedical field.

Notwithstanding, magnesium is highly prone to corrosion, which is one of the major issues and deficiencies that need to be resolved prior to be applied. One broadly employed protection method is coating that, in the case of magnesium, can be made by electrodeposition of another metal, creating a homogeneous layer over its surface and providing corrosion resistance.

Nickel is a commonly used metal for this method but, since magnesium is highly reactive with aqueous solutions, it is frequently necessary to apply pre-treatment processes and/or use a non-aqueous bath for the electrodeposition. Often, these pre-treatment processes are complex and possess hazardous components, such as fluorides and chromium substances.

In this work, a simple and promising approach is employed to perform the nickel electrodeposition on a magnesium substrate. Using a pre-treatment-free procedure and an ethanol electrolytic bath, metallic nickel was successfully reduced from nickel chloride and deposited on a magnesium substrate. Techniques such as X-ray fluorescence (XRF), and scanning electron microscopy (SEM) were used to characterize the deposit.

The coated samples were exposed to air at room temperature and aged. No noticeable evidence of degradation or corrosion was detected. Despite still needing some optimization to increase the amount of deposited nickel, this method seems to be a good pathway to improve the magnesium corrosion, with a more simplified and less-environmentally harmful approach.

Keywords: magnesium, electrodeposition, corrosion

#### **INTRODUCTION**

With a vast range of applications and being the eighth most abundant element, magnesium possesses one of the lowest densities, when compared to other metals, good ductility, high strength of weight ratio and damping capacity, among other properties  $^{1-3}$ . Its variety of applications extends from automotive and spacecraft industries to biomedical technologies  $^{4-6}$ , particularly in the form of alloys, since these may be produced using different combinations to be more suitable for their final purpose, mostly engineering applications <sup>7</sup>.

Despite its good characteristics, magnesium and its alloys have a major flaw, which is their propensity to oxidation. Thus, several techniques have been developed to solve this issue, some relying on surface treatments, alloy modifications, or coatings <sup>8–11</sup>. The latter is a commonly chosen option to mitigate the magnesium corrosion, and it may be accomplished through different methods <sup>9,12,13</sup>. Coating with another metal is denominated as plating and frequently used methods are electroless plating (auto-catalytic) and electrochemical deposition

(electroplating) <sup>14–16</sup>. Nickel is often selected as a coating element, due to its aesthetic appeal, high corrosion resistance and enhancement of other properties <sup>9,17</sup>. Coating magnesium with nickel has been performed in previous studies, but, regardless the chosen method, it is almost indispensable the use of surface pre-treatments to deposit the metal <sup>18,19</sup>.

As mentioned, electrochemical deposition is a recurrent method for plating. This process is based on electrolysis and consists on the reduction of a coating metal, through electrical current, on the substrate to be coated, which acts as the cathode (both are immersed in an electrolytic bath) <sup>20,21</sup>. Due to its high reactivity with water, the use of an aqueous bath for the electrodeposition on a magnesium substrate becomes a challenge. Hence, several studies using complex steps and pre-treatments, as well as alternative non-aqueous electrolytic baths, like ionic liquids and deep eutectic mixtures, were reported <sup>22–25</sup>. Nevertheless, most of these pretreatments use environmentally harmful substances, such as chromium or fluorides, and require many steps to successfully deposit the coating metal <sup>26</sup>.

The aim to find a simple, inexpensive, pre-treatment free and environmentally nonhazardous nickel-plating process was carried throughout this work. Several non-aqueous electrolytic baths were tested, as well as the effect of a simple pre-treatment on the magnesium surface.

## METHODOLOGY

Several endeavours, using different compositions for the electrolytic baths, were carried out, in order to do the electroplating of nickel onto a magnesium substrate. For these trials, pure magnesium rods, with 1.6 mm diameter and purity of 99.9 %, were cut and abraded with 600 and 100 grit sandpaper, before each attempt. These rods were used as the working electrode, in a standard three electrode system, with an electrochemical analysis device, *BASI C3 Cell Stand*, for the obtention of the cyclic voltamogramms of the trials. A silver/silver ion electrode (Ag/Ag<sup>+</sup>NO<sub>3</sub><sup>-</sup>) and a platinum electrode, were employed as the reference and counter electrodes, respectively.

Regarding the electrolytic baths, different compositions were tested using nickel chloride hexahydrate (NiCl<sub>2</sub>.6H<sub>2</sub>O) as the source of nickel. Tetrahydrofuran (THF) and ethanol were the main solvents employed in these experiments, considering that other trials with different solvents were unsuccessful in depositing nickel. Other components, such as potassium hydroxide (KOH), and boric acid (H<sub>3</sub>BO<sub>3</sub>) were added to the electrolytic baths, and the concentrations of each were adjusted to each trial, after preliminary tests. The electrodeposition time was 4000s and the scan rate for the cyclic voltammetry was 100mV/s.

For the pre-treated samples, magnesium rods were firstly immersed in a sodium hydroxide (50 g/L) alkaline bath at 65 °C for 15 min. Afterwards, the samples were rinsed with distilled water and immersed in an acidic bath, with sulfuric acid (20 mL/L) and nitric acid (90 mL/L), for 30 s; the samples were then rinsed with distilled water.

X-ray fluorescence (XRF) and scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) (*INCA Oxford Instruments*), were used as characterization techniques. All SEM images were acquired with a *JEOLJSM-7001F*, equipped with a field emission gun, and 20 kV as the acceleration voltage. Moreover, optical microscopy (*ZEISS Stereo Discovery.V20*) with an amplification of 7,5-150 x, was employed for a better observation of the resulted samples.

#### **RESULTS AND DISCUSSION**

In order to verify if the nickel propensity to be electrodeposited onto the magnesium rod, a cyclic voltammetry experiment (with a minimum of 2 cycles) was performed to each electrolytic bath before electrodeposition. The initial potential used in each cyclic voltamography was adjusted to each trial, to better suit the reduction zone of the nickel compound in that electrolytic bath <sup>27</sup>.

Firstly, it is important to notice the relevance of the boric acid in the electrolytic bath, since without it the nickel coat deposited onto the surface begins to peel off after a few hours, as it can be seen in Fig. 1 and 2, using ethanol and THF as solvents, respectively. Studies from other authors also reported the importance of the addition of boric acid in the electrolytic bath for a successful electrodeposition of nickel <sup>28,29</sup>.



Fig. 9 Magnesium rod after electrodeposition in an electrolytic bath with nickel hexahydrate (0.2 M) in ethanol (after 3 hours)



Fig. 10 Magnesium rod after electrodeposition in an electrolytic bath with nickel hexahydrate (0.2 M) in THF (after 3 hours)

Regarding the effect of the described pre-treatment, tested as an effort to enhance the electrodeposition, after several attempts using different electrolytic baths it was concluded that it did not improve or affect it. Thus, the followed endevedours were performed without the use of any pre-treatment, only the abrasion (with sand paper) of the magnesium rods to remove any oxidated layers or impurities.

After each electrodeposition, all samples were firstly submitted to XRF in order to verify the presence of nickel. If detected, was assumed *à priori* that the nickel was successfully deposited onto the magnesium surface and thus further characterizations were performed. However, due to the geometry of the samples (rods), it was not possible to compare the amount of nickel deposited in each individual trial, and therefore it was not possible with XRF to determine which electrolytic bath composition was the best to achieve the aim of this work.

Fig. 3 and 4 display the cyclic voltammogram (with 4 cycles) and a picture of the resulted sample, respectively, from the electrodeposition with nickel hexahydrate (0.2 M), boric acid (0.4 M) and THF as the solvent. In this trial, accordingly to the cyclic voltammetry, the reduction of nickel occurs between -1300 and 50 mV, therefore the initial potential chosen was -1200 mV. Despite this electrolytic bath composition appear to have only a reduction zone, without oxidation, nickel tretrahydrate and boric acid are hard to dissolve in THF, requiring long periods of time (more than 1 hour, at 65°C with a condensator). Hence, THF was discarded for further trials, being ethanol the preferred solvent, since it easily dissolves the several

components at room temperature. Moreover, ethanol is a greener solvent than THF, making it a better choice for industrial applications.

Nevertheless, some deposition of nickel occurred in this electrolytic bath, as it can be observed in Fig. 4 and will be latter demonstrated by SEM analysis.



Fig. 11 Cyclic Voltammogram for the electrolytic bath with NiCl<sub>2</sub>.6H<sub>2</sub>O (0.2 M)+H<sub>3</sub>BO<sub>3</sub>(0.4 M) in THF. Initial potential: -1200 mV



Fig. 12 Resulting magnesium sample after the electrodeposition. Electrolytic bath: NiCl<sub>2</sub>.6H<sub>2</sub>O(0.2 M)+H<sub>3</sub>BO<sub>3</sub>(0.4 M) in THF

Fig. 5 and 6 exhibit the cyclic voltammogram (with 4 cycles) and a picture of the resulting sample, respectively, after the electrodeposition of nickel, with an electrolytic bath composed of nickel hexahydrate (0.2 M), boric acid (0.2 M) in ethanol and a pellet of potassium hydroxide. The added KOH acts as a supporting electrolyte and slightly increases the initial pH. The boric acid, besides preventing the degradation of the coated samples, also plays an important role as a buffer in the solution  $^{20}$ . In this experiment, the initial potential chosen was -1500 mV, since the reduction zone is between -1800 and -800 mV, accordingly to the obtained cyclic voltammogram.

As it may be observed in Fig. 6, a thin, but homogenous layer was deposited onto the magnesium substrate, when compared to the results obtained with the previous electrolytic bath composition.



Fig. 13 Cyclic Voltammogram for the electrolytic bath with NiCl<sub>2</sub>.6H<sub>2</sub>O (0.2 M)+H<sub>3</sub>BO<sub>3</sub>(0.2 M)+KOH(1 pellet) in ethanol. Initial potential: -1500 mV



Fig. 14 Resulting magnesium sample after the electrodeposition. Electrolytic bath: NiCl<sub>2</sub>.6H<sub>2</sub>O (0.2 M)+H<sub>3</sub>BO<sub>3</sub>(0.2 M)+KOH(1 pellet) in ethanol

After these attempts, a more simple approach was carried out, using an electrolytic bath containing nickel hexahydrate (0.5 M) and boric acid (0.2 M) in ethanol. Figures 7 and 8 exhibit the cyclic voltammogram and a picture of the resulting magnesium substrate, respectively, after the electrodiposition. The obtained cyclic voltammogram (with 2 cycles) reveals that this should be a suitable composition for the nickel electrodeposition, exhibiting a reduction peak close to -1500 mV, and thus an initial potential of -1700 mV was employed. The achieved sample also displays a thin, but homogeneous coated layer, revealing that a simple solution with ethanol as the solvent and a high content of the nickel salt is appropriate for the electroplating.

For the proper characterization of the resulting samples, SEM analysis with EDS, was performed on all electrodeposited materials.


Fig. 15 Cyclic Voltammogram for the electrolytic bath with NiCl<sub>2</sub>.6H<sub>2</sub>O (0.5 M)+H<sub>3</sub>BO<sub>3</sub>(0.2 M) in ethanol. Initial potential: -1700 mV



Fig. 16 Resulting magnesium sample after the electrodeposition. Electrolytic bath: NiCl<sub>2</sub>.6H<sub>2</sub>O (0.5 M)+H<sub>3</sub>BO<sub>3</sub> (0.2 M) in ethanol

From the observation of the SEM images (Fig. 9 and 10), it can be seen that the most successful essay was the one with an electrolytic bath containing KOH, considering that the resulting sample was the only one with a continuous layer of nickel surrounding all the magnesium rod. Notwithstanding, none of the presented samples possess a bright and robust nickel coat, and in most experiments the nickel is found in between oxide layers encircling the magnesium surface, as it could be confirmed by EDS analysis (tables 1 to 6). Thus, the exhibited outside layer in all the tested samples is mainly an oxide layer with cracks, covering the nickel coat.

The deposit obtained using the electrolytic bath containing THF as solvent, barely had any nickel, only a few traces were detected on the surface (Table 1), as it can be observed in Fig. 9 a) and b), and were scattered through the sample.

The simple approach with higher nickel concentration exhibits an almost coutinous nickel layer throughout the surface sample, but also presents several defects, showing that despite having a higher amount of nickel in the electrolytic bath, it did not improve its deposition onto the magnesium sample.

All samples reveal to possess a high amount of oxides, particularly on the outside layer of the coated surface (Tables 1, 3 and 5). The occurrence of oxides indicates the high reactivity

of magnesium with water molecules, present in the solvent and in the salts, that were not previously dehydrated.

Nevertheless, in all presented trials the existence of nickel is verified, indicating that electrodeposition of nickel onto a magnesium surface without any pre-treatment is possible.



Fig. 17 a) and b) SEM pictures (observed in secondary electrons (SEI), magnified at 75x and back-scattered electrons (BSE) mode, magnified at 1000x, respectively) of the resulting sample surface, after the electrodeposition with THF. c) and d) SEM pictures (observed in SEI, magnified at 75x and BSE, magnified at 1000x) of the surface and sectional cut, respectively, of the resulting sample from the electrodeposition with NiCl<sub>2</sub>.6H<sub>2</sub>O (0.5 M) H<sub>3</sub>BO<sub>3</sub> (0.2 M) in ethanol

Table 12. Element composition from EDS analysis of the resulting surface sample from electrodeposition with THF (corresponding to Fig. 9 a))

Element	App Conc.	Intensity Corrn.	Weight%	Weight% Sigma	Atomic%
0	49.39	1.5768	57.18	0.66	69.17
Mg	13.87	0.7115	35.56	0.57	28.31
Cl	0.25	0.7315	0.61	0.16	0.34
Ni	3.05	0.8359	6.65	0.61	2.19
Totals			100.00		

Table 13. Element composition from EDS analysis of the sectional cut from the resulting sample of electrodeposition with THF (corresponding to Fig. 9 b))

Element	App Conc.	Intensity Corrn.	Weight%	Weight% Sigma	Atomic%
Al Ni	1.05 23.72	0.4259 0.9889	9.34 90.66	1.06 1.06	18.31 81.69
Totals			100.00		

Table 14. Element composition from EDS analysis of the resulting surface sample from electrodeposition with NiCl<sub>2</sub>.6H<sub>2</sub>O (0.5 M) H<sub>3</sub>BO<sub>3</sub> (0.2 M) in ethanol (corresponding to Fig. 9

c))

Element	App	Intensity	Weight%	Weight%	Atomic%
	Conc.	Corrn.		Sigma	
0	65.60	1.5977	55.09	0.67	69.98
Mg	13.52	0.6133	29.55	0.53	24.71
Ni	9.71	0.8480	15.36	0.65	5.32
Totals			100.00		

Table 15. Element composition from EDS analysis of the sectional cut of the resulting sample from electrodeposition with NiCl<sub>2</sub>.6H<sub>2</sub>O (0.5 M) H<sub>3</sub>BO<sub>3</sub> (0.2 M) in ethanol (corresponding to Fig. 9 d))

Element	App	Intensity	Weight%	Weight%	Atomic%
	Conc.	Corrn.		Sigma	
0	37.50	1.2746	32.28	0.57	50.77
Mg	15.70	0.5291	32.54	0.49	33.68
Cl	1.09	0.7203	1.66	0.15	1.18
Ni	27.05	0.8855	33.51	0.59	14.36
Totals			100.00		



Fig.18 From left to right: SEM pictures (observation in SEI, magnified at 75x for the first picture and BSE for the remaining images, magnified at 170x and 1000x, respectively) of the magnesium sample surface and sectional cut from the electrodeposition with KOH

Table 16. Element composition from EDS analysis of the resulting surface sample fromelectrodeposition with KOH (corresponding to Fig. 10 left)

Element	App	Intensity	Weight%	Weight%	Atomic%
	Conc.	Corrn.		Sigma	
0	57.62	1.4567	49.78	0.52	61.42
Mg	28.69	0.7953	45.38	0.50	36.85
CĨ	0.27	0.7164	0.48	0.11	0.27
Ni	2.90	0.8370	4.36	0.41	1.47
Totals			100.00		

Table 17. Element composition from EDS analysis of the resulting surface sample from electrodeposition with KOH (corresponding to Fig. 10 image on the middle and on the right)

Element	App	Intensity	Weight%	Weight%	Atomic%
0	Conc. 136 79	Corm. 1 5677	55.04	O 38	69.21
Mg	31.97	0.6400	31.50	0.30	26.07
CĨ	0.55	0.7339	0.47	0.09	0.27
Ni	17.40	0.8452	12.98	0.32	4.45
Totals			100.00		

# CONCLUSIONS

Throughout this work, several endeavours were carried out to deposit nickel onto pure magnesium, via electrodeposition, with the aim to find a simple and greener process without the use of pre-treatments. Several electrolytic baths were tested, maintaining nickel chloride hexahydrate as the source of nickel. Given the high reactivity of magnesium with water, a non-aqueous solvent is necessary to be employed if no pre-treatments are used. Thus, it was observed that ethanol is a suitable solvent for the electrodeposition, since it can easily dissolve the different components and carry out the electrodeposition at room temperature. Moreover,

boric acid demonstrated to be a crucial part of the electrolytic bath, as it prevents the quick degradation of the coated layers in the samples.

The electrolythic bath that revealed more promising results (through the analysis of SEM/EDS and microscopic observation) was composed of nickel hexahydrate (0.2 M), boric acid (0.2 M) and potassium hydroxide (1 pellet). With this trial, a continuous thin nickel layer deposited onto magnesium. However, the presence of oxide layers surrounding the sample substrate is noticeable in all tested experiments.

Hence, as further work, this process still needs optimization, in order to prevent the appearance of the oxide layers. New experimental conditions should be tested, such as adjusting the concentration and/or dehydration of all the components, or performing the trials under inhert atmosphere.

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# FABRICATION OF 3D MICROSTRUCTURES FOR PHOTOCATALYSIS

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#### ABSTRACT

In contemporary times, there is a need for efficiency-enhancing materials due to the escalating consumption of energy. One well-studied material is titania (TiO<sub>2</sub>) which is used in various energyrelated scientific disciplines. The present work focuses on the fabrication of three-dimensional (3D) microstructures consisted of TiO<sub>2</sub> nanorods for the investigation of their photocatalytic performance. The purpose is to increase the active surface area of the nanorods for interaction with their environment enhancing the phenomenon of photocatalysis. Firstly, a hybrid organic-inorganic material (SZ2080<sup>TM</sup>) is synthesized via the sol-gel method. Secondly, the MultiPhoton Lithography (MPL) technique is used for the fabrication of the desired 3D scaffolds serving as substrates for growth of TiO<sub>2</sub> nanorods. The 3D structures are at microscale with various shapes. In this work the structures that are mainly investigated are of spherical or cylindrical symmetry. Essential condition for being substrates is that, the 3D structures undergo a heat treatment step. This method results in the removal of the organic part, leaving microstructures that mainly consist of a ceramic-like material. The heat treatment also results in a shrinkage of the actual size of the 3D microstructures which was calculated to be about (40-50)% of their initial size, depending on the apllied temperature. The aim of this work is to study the optimal way to remove the organic part from 3D microstructures minimizing their dirstortion in order to use them as substrates for subsequent growth of  $TiO_2$  nanorods. In this way, the increase of active surface area can be exploited in maximum way.

Keywords: MPL, 3D microstructures, PLD, TiO<sub>2</sub>, nanorods, photocatalysis

### **INTRODUCTION**

Nowadays there is a plethora of scientific projects in the research field of photocatalysis such as self-cleaning surfaces, air purification, water treatment, water splitting and photoelectrochemical conversion [1]–[6]. This is because photocatalysis promises a solution to the expanding energy demand since it is based on exploitation of a renewable energy source. During this procedure [7], photons from solar irradiation, are harvested resulting in the desired chemical reactions. This work refers to heterogeneous photocatalysis in which the catalyst, reactants and products occupy different phase. When a semiconductor is illuminated by photons whose energy is equal to or greater than its band-gap energy, there is absorption of these photons resulted in electron-hole pairs. These pairs dissociate into free electrons and holes in the conduction and valence band respectively.

Currently, the research for materials in order to enhance photocatalytic performance is rapidly expanding. Semiconductors are being investigated for their efficiency as catalysts in heterogeneous photocatalysis. It is pivotal the fact that they have band-gap energies within solar spectrum for efficient photons harvesting. Moreover, they must be mechanically and chemically stable under extreme conditions with an eco-friendly impact to the environment. TiO<sub>2</sub> [8] is the most common semiconductor which has been used for this purpose as it is commercial available, a low cost, non-toxic and easily handled material. In nature it mainly occurs in crystalline phases of rutile, anatase and brookite with a band-gap energy of 3, 3.2, 3.15eV respectively in their bulk form. Although its band-gap energy is a disadvantage related to solar spectrum, there is a way to tackle it. It is observed that nanosized titanium dioxide structures exhibit more efficient photocatalytic process as surface area is increased. Consequently, photocatytic performance is enhanced and that is why there is an abundance of scientific research for nanosized titania structures last years [9].

The purpose of this work is to fabricate 3D microstructures which could be used as substrates for subsequent growth of  $TiO_2$  nanorods. It is expected that if the active surface area increase [10], this will result in enhancement of photocatalytic performance. By minimizing the distortion of 3D microstructures after thermal treatment, these microstructures are used more beneficially as substrates since there is more available surface in which nanorods can be synthesized.

#### METHODOLOGY

Firstly, a standard sol-gel technique [11] was used to synthesize the desired hybrid organic-iorganic material SZ2080<sup>TM</sup>. The aim is to form an inorganic network inside of a photopolymerizable material. It is based on the idea that the combination of two or more materials with different functionalities can give new hybrid materials with the desired properties. In addition, the presence of a photoinitiator is significant in order to absorb the incident light initiating the polymerization process. The first step of the sol-gel method is hydrolysis and condensation where organic monomers and inorganic materials are mixed with water to form a porous interconnected cluster structure. Either an acid like hydrochloric acid (HCL) or a base like ammonia (NH<sub>3</sub>) can be employed as a catalyst. As monomer units are utilized 3-(trimethoxysilyl) propyl methacrylate (MAPTMS, 99%, Sigma-Aldrich) and methacrylic acid (MAA, >98%, Sigma-Aldrich) and as inorganic unit zirconium propoxide (ZPO, 70% in propanol, Sigma-Aldrich) is used. The next step is gelation, where trapped water molecules are removed from the network. This can be done by drop casting the liquid form material onto conventional glass coverslips and were left under vacuum conditions for at least 4-5 hours to form a gel. To promote the structure adhesion, the coverslips were previously coated with the organic monomer compound MAPTMS.



Fig. 1. Schematic illustration of processing flow. Firstly, a standard sol-gel technique is used in order to synthesize the hybrid material and then MPL technique is utilized to fabricate the 3D microstrures via two photon polymerization (TPP)

Secondly, the MPL technique [12] was utilized in order to fabricate the desired 3D structures by polymerizing the above material selectively in three dimensions. This is because the polymerization occurs only in a volument element called "voxel" inside a photopolymerizable material. This characteristic comes from the fact that polymerization takes place due to multiphoton absorption of incident laser beam by the material. This only happens inside the focal volume of a objective lens, where high light intensities are created [13]. Also, it is pivotal the fact that, femtosecond pulse duration coupled with high frequency repetition rate are required in order to achieve high light intensities which can result in mutiphoton absorption by the material more efficiently. Therefore, the chemical reactions of polymerization are taken place only in voxel, leaving unaffected the rest of the material. One more thing which is important is that when polymerization process is occurred, a liquid or gel-state material is converted into a solid state one. Thus, in-volume patterning can be achieved with fabrication resolution more than 100nm. Many factors affect the fabrication resolution such as the objective lens used to focus the laser beam into the material, the incident light intensity of laser beam, the exposure time of irradiation and of course material itself. MPL comprises the most appropriate 3D fabrication technique, since it can imprint any desired 3D morphology in the micrometer scale.

The energy source is a femtosecond laser operating at 780nm, which typically produces pulses with duration 130fs. Its repetition rate is 80MHz and its output power is around some hundreds of Watts. A series of mirrors is employed in order to direct the laser beam via optical components to the sample. Also, there is an attenuator which is used to adjust the light intensity as it is connected with a computer. Online monitoring of fabrication process is achievable via a dichroic mirror and a CCD camera. The dichroic mirror located just before the objective lens and reflects the incoming laser beam but allows green light from a led. In this way the sample is illuminated by a led located underneath of the sample during fabrication process. Because of the difference in refractive index of light between the polymerized and the unpolymerized material, an image is created in real time via a CCD camera, which is located behind the dichroic mirror and is connected with a computer.



Fig. 2. Visual illustration which shows how a laser beam is focused by an objective lens in order to irradiate a sample. To avoid distortion that laser beam can cause, the sample is localised bottom up

After the photopolymerization, a process called development was taken place where samples were immersed in a solution consisting of 1:1 4-methyl-2-pentanone/isopropanol for 15 min, washed with isopropanol for another 15min, and then allowed to air dry. The goal of this step is the removal of unpolymerized resin leaving the desired 3D microstructure. This is feasible as the hybrid material used is a negative photoresist. In this case, the absorption of light irradiation results in the cross-linking of the polymer chains, making the exposed area insoluble to an appropriate solvent used to remove the unpolymerized material.

Next, the fabricated microstructures underwent a heat treatment step [14]. Thermal treatment is a vital step for this work as there is the need for removal of the organic part of the structures in order to achieve the growth of  $TiO_2$  nanorods on 3D microstructures in next steps. Therefore, the purpose is to find out an efficient way to remove the organic part minimising the distortion of 3D structures which is crucial for their subsequent role of structures as substrates for  $TiO_2$  nanorods. The 3D microstructures were located in a furnace where a series of experiments was carried out. In particular, the structures were heated up from room temperature to the desired temperature with constant rate, left for 1 hour and then were cooled down with the same constant rate. The constant values of the temperatures which were selected for this series of experiments were between  $(500-1100)^{\circ}C$  and a rate of 2°C/minute was used for the organic part of the structures be achieved due to the break of bonds of carbon as the temperature rose. Therefore, a shrinkage of the actual size of the structures was resulted in after the removal of carbon making those structures to have been consisted of a ceramic-like material.

#### **RESULTS AND DISCUSSION**

Scanning Electron Microscopy (SEM) images of the 3D microstructures fabricated via the MPL technique are shown in Figure 3. Synthesis of hybrid organic-inorganic material SZ2080<sup>TM</sup> without methacrylic acid was previously taken place in order to be used in MPL technique. Figure 3 shows whole 3D structure, which is fabricated via MPL. Its lattice can be observed, which is comprised of cylinders that can be seen side by side. Also, there is a side view of the structure where it can be observed that this microstructure is consisted of cylinders supported by legs. The aim is to fabricate 3D microstructures which have large surface area and at the same time they endure the subsequent fabrication techniques in order to be substrates for growth of TiO<sub>2</sub> nanorods. Therefore, it is substantial to study the construction of durable the desired geometry/morphology but also evaluate structures with how their geometry/morphology is affected by heat treatment which is essential fabrication step for the accomplishment of this work. A study was carried out where the results of the thermal treatment were evaluated in order to conclude to the final designs structures which should be fabricated.

In this work, experiments were conducted on how a range of applied temperatures affect the structure's shrinkage. It is found that the size of final structure is decreased with the rise of the applied temperature. In Figure 4 the above 3D structure is depicted, for evaluation of its shrinkage after thermal treatment. The microstructure was heated up with a constant rate of 2°C/min from room temperature to 700°C, it is left at this temperature for 1 hour and then it is cooled down until room temperature with the same rate. It is clearly illustrated that its shrinkage as a result of the removal of organic part and by measuring its dimensions, it was found that the final structure is about 62-66% of the initial size. Also, it was measured that the final structure is about 53-57% of the initial size when the same experiment was carried out at 1100°C. These outcomes are anticipated since it is more likely to break bonds when the temperature increases.



Fig. 3. SEM images of a 3D microstructure via the MPL of the SZ2080<sup>TM</sup>. (a)Top view, (b) Magnification view of the structure, (c) Higher magnification, (d) Side view



Fig. 4. SEM images of a 3D microstructure after thermal treatment at 700°C for 1 hour. (a)Top view, (b) Magnification view of the structure, c) Higher magnification, d) Perspective view

Various other morphologies were tested for their deformation after thermal treatment. They were selected as they possess morphology with high surface to volume ratio. In this way they are more efficient to enhance photocatalysis as substrates. An example can be observed in Fig. 5, where another 3D microstructure is presented. It can be confirmed that 3D structures with a spherical or cylindrical symmetry withstand the thermal treatment in contrast to structures with other morphology after same experiments were carried out.

In the cases of 3D structures without spherical or cylindrical symmetry or 3D structures without legs, it was not be able to evaluate the shrinkage as these structures were largely deformed or collapsed. A reasonable explanation is that there is non-uniform removal of the organic part resulted in the great deformation of these structures. For the same concept in the case of absence of legs, the interaction with the structure's substrates is occurred so the deformation of structures is not affected only by the removal of organic part. To infer, the study shows that, microstructures supported with legs and spherical or cylindrical symmetry heated up to 700-800°C with the aforementioned experimental conditions give the desired results for the goal of this work.



Fig. 5. SEM images of a 3D microstructure after thermal treatment at 1100°C for 1 hour. (a)Top view, (b) Magnification view of the structure, c) Higher magnification, d) Side view

Furthermore, Energy Diverse X-ray (EDX) spectroscopy was utilized in order to quantify the removal of the organic part and to study the composition of 3D microstructures before and after thermal treatment. A series of experiments were conducted where EDX spectra were recorded from 3D microstructures with different morphologies, which were previously undergone thermal treatment. It is found that the morphologies of 3D structures do not affect the outcome of the experiments so the only distinguishable factor is the applied temperature. Figure 6 illustrates the stoichiometric composition of 3D microstructures before and after thermal treatment, under applied temperatures of 1000°C and 1100°C for 1 hour. The existence of the gold (Au) is not related with the material but it is necessary for the implementation of the characterization methods. In Fig. 6 it is deduced that as the applied temperature increases, the percentage of carbon in material decreases due to the burning of the organic part. As a result, the percentage of all other elements increases due to the fact that the ratio of all elements in the material is constant. Also it can be observed that, there is only one peak which corresponds to electronic transitions for two minerals of zirconium (Zr) and Au. The reason for that is because characteristic electronic transitions of Zr and Au (2.04 and 2.12keV respectively) are close enough to cannot be distinguished by the experimental set up



Fig. 6. EDX spectra on 3D microstructures before and after thermal treatment for 1 hour

# CONCLUSIONS

The purpose of this work is not accomplished as all fabrication steps have not been carried out by now. Nevertheless, the study in order to remove the organic part of 3D microstructures has been thoroughly investigated. It has been studied how to synthesise the desired hybrid material which is used for photopolymerization and also how to fabricate the desired 3D structures implementing the MPL technique. In addition, it was found that 3D structures of spherical or cylindrical symmetry were more durable during the heat treatment step, than those with other morphologies. A series of experiments was carried out in order to set the appropriate conditions that give the desired results for the aim of this work. To infer, the study confirms the conclusion that 3D microstructures with legs and spherical or cylindrical symmetry heated up to 700-800°C with the experimental conditions described, give the desired results since the removal of the organic part is minimizing the deformation of 3D microstructures. In particular, it is measured to be about 50-60% of their initial size for the above experimental conditions. As a result, the final 3D structures are mainly consisted of a ceramic-like material which made them appropriate as substrates for the subsequent fabrication methods. After implementation all the fabrication steps it is expected that the active surface area of titania nanorods increase result in enhancement of photocatalytic performance.

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# FERROELECTRIC PROPERTIES OF COBALT DOPED LEAD FERRITE THIN FILMS SYNTHESIZED BY REACTIVE MAGNETRON SPUTTERING

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#### ABSTRACT

Multiferroics have unique properties - the coexistence of at least two primary ferroic states including ferroelectricity, ferromagnetism, and ferroelasticity. The focus has been on materials, which are characterized by simultaneous ferroelectricity and ferromagnetism. One such material is lead ferrite (Pb<sub>2</sub>Fe<sub>2</sub>O<sub>5</sub>), in which a magnetoelectric effect occurs. This effect makes it possible to control the magnetic properties with electric field and vice versa. It is this feature that is very attractive in the development of the latest technologies such as low-power, novel solid state memory applications, functional and green nanoelectronics. We were able to synthesize lead ferrite thin films by reactive magnetron sputtering, which exhibited both ferroelectric and magnetic properties at room temperature. Cobalt was chosen as the dopant to obtain films with better dielectric and structural properties, thus cobalt doped lead ferrite has been synthesized *in situ* in the temperature range of 500 – 600 °C. Structural and dielectric properties were investigated which showed that introduction of cobalt into the lattice could have led to its distortion, thus increasing non-centrosymmetry. Comparing undoped lead ferrite with cobalt doped samples the improvement of ferroelectric properties was observed, where the remnant polarization increased from 54  $\mu$ C/cm<sup>2</sup> to 68  $\mu$ C/cm<sup>2</sup> and coercive field changed from 68 kV/cm to 86 kV/cm.

Keywords: Multiferroic, lead ferrite, magnetron sputtering, cobalt doped.

#### **INTRODUCTION**

Multiferroics exhibit more than one primary ferroic property. One of the most interesting property is magnetoelectric effect which combines ferroelectric and magnetic orders. Occurring simultaneously these properties result in a coupling and possible manipulation of each other. For instance, switching of magnetic polarization could be controlled by electric field and vice versa. Recent advances in utilizing multiferroic materials allow making memory technologies (FeRAMs, MRAMs), various sensors, photovoltaic, energy harvesting technologies [1-6]. Multiferroics as a multifunctional material improve multiple field addressable memory which are created to increase data storage density thus leads to saving of natural resources [1]. Additionally, multiferroics might improve photovoltaic technologies since these materials are band gap dependent, consequently overcome the efficiency of Shockley-Queisser limit [7]. Recent studies showed possibility to use multiferroic materials in hydroelectric cells to produce green electricity by dissociating water molecules at room temperature [8]. Due to its complexity multiferroics are very rare in nature. Also, part of this group of materials only exhibits multiferroic effect at lower than room temperature, therefore, the application of these materials is also limited in practice. Another issue related to these materials is complex mechanism of multiple properties coexistence in the same phase which leads to difficult material engineering processes [1, 9].

 $BiFeO_3$  (BFO) is the most widely studied multiferroic due to its suitable characteristics for using in the multifunctional materials, large Neel temperature (~640 K) and high ferroelectric transition temperature (~1100 K). In spite of these characteristics BFO exhibits low magnetoelectric effect coupling which limits application of this materials [10]. Considering all these limitations, there is a high demand for new multiferroic materials and improvements of the current ones. Min Wang et al. has reported about lead ferrite  $Pb_2Fe_2O_5$  (PFO) multiferroic properties [11]. Drawing attention to another prospective multiferroic material. This material possesses ferroelectric characteristic due to lone paired electrons (Pb<sup>+2</sup>) and ferromagnetic behaviour by reason of the presence of partially occupied d-orbital (Fe<sup>+3</sup>). Importantly, PFO has these properties at room temperature.



Fig. 1. Pb<sub>2</sub>Fe<sub>2</sub>O<sub>5</sub> thin film synthesized at 500 °C hysteresis family measured with external electric field up to 12,5 V at 50 Hz [12]

Our research group has researched PFO thin films synthesized by reactive magnetron sputtering. During this research we confirmed that PFO exhibits ferroelectric properties. In Fig. 1 P-E measurements display ferroelectric properties with remnant polarization of ~54  $\mu$ C/cm<sup>2</sup> and coercive field ~68,6 kV/cm at applied external field of 12,5 V (50 Hz) [12].

P-E measurements showed unsaturated hysteresis loops which could be affected by the leakage currents in thin film samples as a result of impurities, non-stoichiometric and presence of defects. Hence there is a need for improving of this material which could be achieved by chemical substitution. For this purpose, we have selected cobalt ions as dopants. Fe<sup>3+</sup> ions are substituted by Co<sup>3+</sup> ions which have similar ionic radius of 0.645 Å and 0.61 Å respectively. Many studies have been conducted on the influence of cobalt on multiferroic materials. It is reported that cobalt substitution improves both ferroelectric and magnetic properties. Larger remnant polarization could be due to structural distortion induced by doping of Co [13-15].

In this work Co doped PFO thin films were synthesized by reactive magnetron sputtering. This synthesis method has been chosen due to the capability of forming high quality thin films. Furthermore, it is a solution-free method which means environmentally friendly.

# METHODOLOGY

Cobalt doped lead ferrite samples were synthesized by *in situ* layer-by-layer reactive magnetron sputtering. Before the formation of PFO, a seeding layer of Ti was deposited with the same synthesis method. Platinized silicon was used as substrate (Pt/Ti/SiO<sub>2</sub>/Si). The thickness of Pt, TiO<sub>2</sub> and SiO<sub>2</sub> layers are 200 nm, 50 nm and 1  $\mu$ m respectively. For lead ferrite formation oval shaped, flat cathodes (for each element – Pb, Fe and Co) with purity of 99,95% were used. Seeding layer of Ti is formed at temperature of 750 °C in argon gas environment with a pressure of 1,3 Pa. The thickness of this layer is ~7 nm. After titanium synthesis temperature was lowered to 500 °C, the argon environment was changed to oxygen. Formation of PFO layer in O<sub>2</sub> environment at 1,3 Pa took 2 minutes to form layer with thickness of 20 nm.

Doping of PFO with cobalt was performed in the 500 – 600 °C temperature range and O<sub>2</sub> gas environment for 1 hour. The flux of cobalt ions during synthesis was controlled by slit above Co magnetron. The distance between cathodes and substrate was 60 mm. After the deposition, to form capacitors the aluminium electrodes with 1,3 mm in diameter were synthesized using thermal evaporation method. X-ray diffraction (XRD) patterns of the PFO films were registered with a Bruker D8 series diffractometer using monochromatic CuK $\alpha$  radiation with Bragg-Brentano geometry. The ferroelectric hysteresis loop measurements of films were examined using Sawyer and Tower method (resistance of 1 k $\Omega$  and reference capacitor of 150 nF was used in the circuit at 50 Hz frequency and 25 °C).



Fig. 2. Setup of magnetron system

The schematic of magnetron and sample setup is shown in Fig. 2., where: 1 - substrate (platinized silicon), 2 - sample holder and heating element, 3 - direction of movement to maintain layer-by-layer thin formation, 4 - cathodes (each for individual element), 5 - cooling system, 6 - DC power source for magnetrons.

Synthesis temperature range has been selected to be 500 - 600 °C. It is based on previous PFO studies [12]. Cobalt fraction in  $Pb_2(Fe_{1-x}Co_x)_2O_5$  films was selected to be x = 0,03, 0,04. The parameters of magnetrons are listed in Table 1. The required magnetron parameters were calculated by using amount of material formula:

$$v = \frac{N}{N_A},\tag{1}$$

where:  $\upsilon$  – the amount of material (mol); N – the number of molecules; N<sub>A</sub> – Avogadro constant (6,02 · 10<sup>23</sup> mol<sup>-1</sup>)

Cathodes	Elements					
Cathode par.	Pb	Fe	Co			
Discharge current, A	0.38	2.00	0.30			
Discharge voltage, V	293	275	265			

Table 1. The parameters of magnetrons

#### **RESULTS AND DISCUSSION**

# **XRD** analysis



Fig. 3. XRD pattern of the x=0,03 Co doped Pb<sub>2</sub>(Fe<sub>1-x</sub>Co<sub>x</sub>)<sub>2</sub>O<sub>5</sub> thin film synthesized at 550 °C

For x=0,03 cobalt doped lead ferrite sample synthesized at 550 °C X-ray diffraction measurement is shown in Fig. 3. The strongest peak at 40° is attributed to platinum. PFO diffraction peaks (2 2 0), (3 1 2), (4 0 0) and (4 2 4) were observed at 32°, 38°, 46° and 56° respectively. Such structures were observed and identified as monoclinic by Joke Hadermann et al. [16]. Another research group led by Min Wang et al. [17] reported the similar results. Along with PFO peaks PbO and Fe<sub>2</sub>O<sub>3</sub> phases are observed as well. PbO peaks occurred at 30°, 31°, 35°, 36°, 37°, 45° and 54°, where Fe<sub>2</sub>O<sub>3</sub> only at 34°. During his research Min Wang et al. synthesized PFO using different ratio of Fe<sub>2</sub>O<sub>3</sub> and PbO and reported that unwanted phases in this case Fe<sub>2</sub>O<sub>3</sub> and PbO could not be avoided possibly due to crystallographic shear structure and similar oxidation states [17].

# **P** – **E** measurements

P-E hysteresis measurements (Fig. 4) show ferroelectric behaviour in all samples. Fig. 4 a) shows the polarization dependence on applied external electrical field of PFO with x=0,03 cobalt doping at 500 °C. The obtained remnant polarization (P<sub>r</sub>) reaches up to 40,6  $\mu$ C/cm<sup>2</sup> and coercive field (E<sub>c</sub>) ~48,6 kV/cm. Increase of synthesis temperature changes thin film's ferroelectric properties. In Fig. 4 b) the sample formed at 550 °C obtained remnant polarization (P<sub>r</sub>) of 65,4  $\mu$ C/cm<sup>2</sup> and coercive field (E<sub>c</sub>) ~102,9 kV/cm. Further increase in synthesis temperature had a negative effect on thin films. Sample in Fig. 4 c) shows hysteresis loop of PFO thin films formed at 600 °C. The remnant polarization slightly decreased to 60,9  $\mu$ C/cm<sup>2</sup> and coercive field value to 88,6 kV/cm. This could be due to structural phase transitions, which would change the direction of spontaneous polarization, or it could be related to the formation of secondary phases [13]. The obtained oval-shaped hysteresis are evidence of incomplete saturation, which could indicate leakage currents in the samples. Varying oxygen states of Fe<sup>2+</sup> and Fe<sup>3+</sup> affect the appearance of oxygen vacancies, and both the presence of Fe<sup>2+</sup> and oxygen vacancies leads to higher leakage currents in the capacitor [14, 18].



Fig. 4. P-E hysteresis family of x=0,03 Co doped Pb<sub>2</sub>(Fe<sub>1-x</sub>Co<sub>x</sub>)<sub>2</sub>O<sub>5</sub> thin films synthesized at: a) 500 °C; b) 550 °C; c) 600 °C and x=0,04 Co doped Pb<sub>2</sub>(Fe<sub>1-x</sub>Co<sub>x</sub>)<sub>2</sub>O<sub>5</sub> thin films synthesized at: d) 500 °C; e) 550 °C; f) 600 °C

Fig. 4 d) to f) shows the room temperature hysteresis loops (P-E) measured at 50 Hz of x=0,04 Co doping PFO thin films at 500 - 600 °C temperature range. As seen in Fig. 4 d) the sample synthesized at 500 °C shows a ferroelectric property with an unsaturated loop due to high leakage current density. The remnant polarization (P<sub>r</sub>) reaches up to 20,3  $\mu$ C/cm<sup>2</sup> and coercive field (E<sub>c</sub>) ~28,6 kV/cm. Similar changes in properties are observed as in the previous samples, where ferroelectric properties improved with higher synthesis temperature. Film formed at 550 °C (Fig. 4 e)) demonstrates P<sub>r</sub>~31,6  $\mu$ C/cm<sup>2</sup> and coercive field (E<sub>c</sub>) ~37,1 kV/cm. Further increase in synthesis temperature improves ferroelectric properties, unlike in previous x=0,03 Co samples. Co doped PFO synthesized at 600 °C (Fig. 4 f)) exhibits significant increase in P<sub>r</sub> which reaches up to 65,4  $\mu$ C/cm<sup>2</sup> and coercive field to 85,7 kV/cm. Although ferroelectric properties improved, the obtained P-E hysteresis remained unsaturated due to leakage currents.

Fig. 5 displays the remnant polarization and coercive field dependence on cobalt content in PFO samples comparison. The undoped PFO ferroelectric properties from our previous research [12] where obtained highest remnant polarization ~54  $\mu$ C/cm<sup>2</sup> was also included in the comparison. It shows that ferroelectric properties deteriorate with the increase of Co concentration. Even though both coercive field value and remnant polarization decreased in all

samples, film synthesized at 600 °C with x=0,04 Co stands out and exhibits highest  $P_r$  at 65,4  $\mu$ C/cm<sup>2</sup>. Ferroelectric properties of PFO thin films are affected by factors such as phase purity, orientation and leakage currents. Enhancement of these properties could be achieved due to increase of lattice distortion, which leads to increase in spontaneous polarization as well. These properties may also have been affected by different size of dopant ions, which results in larger off-centre ion position in the Fe-O octahedron [19].



Fig. 5. Remnant polarization and coercive field dependence on cobalt content and synthesis temperature in Pb<sub>2</sub>(Fe<sub>1-x</sub>Co<sub>x</sub>)<sub>2</sub>O<sub>5</sub> films

# CONCLUSIONS

Co doped PFO were successfully synthesized at 500 - 600 °C temperature range by in situ layer-by-layer reactive magnetron sputtering at pure oxygen environment. The Co content have been selected to be x=0,03 and 0,04. XRD measurement shows formation of lead ferrite phases even when the formation of unwanted PbO and Fe<sub>2</sub>O<sub>3</sub> phases was not avoided. All samples have shown ferroelectric behaviour. P-E hysteresis measurements were performed and indicated the best ferroelectric properties with remnant polarization of 65,4  $\mu$ C/cm<sup>2</sup> and coercive field of ~85,7 kV/cm obtained in sample with cobalt x=0,04 which was synthesized at 600 °C. Although thin films show an enhanced ferroelectric properties, hysteresis loops were oval shape and have not saturated completely due to leakage current in the capacitor. The deterioration of ferroelectric properties with the increase of temperature was observed at samples with Co x=0,03. This could be due to structural phase transitions and formation of secondary phases. The obtained data are promising, therefore the measurements of dielectric and magnetic properties will be performed in the future as well as the structural research of films. Also, the different cobalt content will be investigated.

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# CARBON AND GOLD AS EFFECTIVE DIFFUSION BARRIERS FOR CU<sub>11</sub>MN<sub>1</sub>SB<sub>4</sub>S<sub>13</sub> TETRAHEDRITES

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#### ABSTRACT

In this work, the possibility of using carbon and gold as effective diffusion barriers for thermoelectric tetrahedrites was investigated. C and Au layers were set on  $Cu_{11}Mn_1Sb_4S_{13}$  tetrahedrite substrates by hot-pressing and thermal evaporation techniques, respectively. The materials were aged at 648 K during 500 h and analysed by X-ray Diffraction (XRD) and Scanning Electron Microscopy complemented with Energy Dispersive Spectroscopy (SEM-EDS). SEM-EDS observations indicate the absence of secondary phases in the aged materials. However, in the gold layer a considerable amount of copper was detected, suggesting the interdiffusion of this element from the tetrahedrite matrix/substrate towards the gold. On the other hand, copper in excess was found in the tetrahedrite matrix close to the carbon layer, pointing to the possibility of sulphur sublimation during the aging tests. The addition of carbon and gold layers to the tetrahedrite substrates resulted in crack free interfaces and suggest a good match between the coefficient of thermal expansion (CTE) of both materials (coatings and substrates). Thermal stress simulations support the referred results, with low stresses being observed at the interface between the coatings and substrates. Contact resistance measurements display a low resistance between the tetrahedrite material and electrical contacts, pointing to a successful use of carbon as a diffusion barrier.

Keywords: Thermoelectric materials; Tetrahedrites, Diffusion barriers, Hot-pressing, Thermal evaporation, Aging tests

#### **INTRODUCTION**

Thermoelectric generators (TEG's) can directly convert heat into electricity through the Seebeck effect [1]. These devices are based on modules constituted by thermoelectric (TE) p- and n-type semiconductor materials, usually electrically connected in series and thermally connected in parallel [2]. Typically, the semiconductor materials are connected between each other through copper or aluminum electrodes to the electric circuit for power generation. The TE materials are fixed to the electrodes by soldering or brazing [3], [4], although hot pressing and spark plasma sintering can be used as well as efficient techniques for jointing fabrication [5]–[8].

The TE performance of a material is evaluated through its dimensionless figure of merit,  $zT = S^2 \sigma T/\kappa$ , where S represents the Seebeck coefficient,  $\sigma$  is the electrical conductivity, T the absolute temperature and  $\kappa$  the thermal conductivity [9]. In recent years, innumerous studies were reported on the development of new materials with improved zT, but just a few were published on the development of TE modules. However, the improvement of such devices is critical not only for the practical use of TE materials, but also to justify their basic research. To advance on the development of TE modules, many crucial aspects must be taken into account. One of these aspects is the nature and quality of the interface between the TE material and the solder/electric contact. Electrical and thermal contacts with large resistivity can ruin the device performance, even if materials with good TE properties are used. Moreover, the growth of interfacial phases by solid state reaction can occur by inter-diffusion of elements between the TE material, electric contacts, and/or solders [10]. These phases are usually brittle, with coefficients of thermal expansion (CTE) and electrical properties significantly different from the base TE materials. The presence of such compounds at the joints usually leads to the appearance of cracks and voids that damage the interfacial bonding strength and deteriorate the electrical properties/contacts, resulting in a loss of efficiency and eventually on the failure of the TE module [11]. Therefore, their formation must be avoided, which can be done by employing diffusion barriers. Depending on the type of TE material, Bi-Te based, Ge-Te based, Pb-Te based, skutterudites-based, half-Heusler (HH) or Silicides, different diffusion barriers can be used. Metals and alloys, like Ni, Co, Mo, Ti, Al-Si, Co-P etc., are the most used materials for diffusion barriers [10]–[15], given their good/high electrical and thermal conductivity. For example, nickel is a largely used diffusion barrier, especially on commercial Bi<sub>2</sub>Te<sub>3</sub>-based TEG's [15]. Still, several studies report that nickel migrates to the TE material through the successive cycles of use, especially at the joints exposed to high temperatures [11], [15]–[17].

Commercial TE devices use materials developed until the 60's that contain rare and toxic elements (like Bi, Te or Pb) and exhibit small efficiencies (<10%) [18]. To change that tendency, a new generation of TE materials is now under study, combining cutting-edge approaches to increase zT through band engineering [19]–[21]. One family of such new materials, seen with great potential for TE applications, are the tetrahedrites (coper antimony sulfosalts) [22], [23]. These materials are based on cheap, abundant, and low-toxicity elements. They have a  $Cu_{12-x}(Zn,Fe,Ni,Mn,Co)_xSb_4S_{13}$  general formula and present high positive Seebeck coefficients [24], crystallizing in a complex cubic structure that is composed by 58 atoms per unit cell, space group *I-43m*, which results in a characteristic low  $\kappa$ . Several compositions have zT's close to unit at temperatures  $\geq 623$  K, making tetrahedrites one of the lead-free bulk sulfides with the highest TE performance between 298 K<T<623 K [22], [25], yet, TE devices based on these materials are still under development. Given their nature, tetrahedrites have a limited thermal stability and a high chemical reactivity at medium temperatures, oxidizing in air and reacting with other elements and compounds if in contact for long periods [9], [26]–[28]. Consequently, studies are needed, being particularly critical the ones on the diffusion barriers between tetrahedrites and the other materials, as those of electrical contacts or solders, where metallic sulfides can be formed. To avoid degradation, it is necessary to identify the best layers for diffusion barriers, capable of avoiding those chemical reactions.

Here, we present the investigation of carbon and gold layers as diffusion barriers for Cu<sub>11</sub>Mn<sub>1</sub>Sb<sub>4</sub>S<sub>13</sub> tetrahedrites, materials that already present high thermoelectric efficiencies, average zT>0.4 in 298-623 K and zT>0.7 at 623 K [29]–[32]. The objective is to evaluate the effectiveness of these layers by investigating the inter-diffusion of elements and existence of new phases, cracks and/or surface detachments after 500 h of exposition to 648 K under vacuum conditions. Cu<sub>11</sub>Mn<sub>1</sub>Sb<sub>4</sub>S<sub>13</sub> tetrahedrites were chosen given the good TE performance (average zT>0.4 in 298-623 K) and based on a series of multiple works that our group has been performing to develop cheap and low toxic thermoelectric systems to be used in real applications [32], [33]. In the referred works, the thermal stability, oxidation resistance, protective coatings and the effect of composition and sintering conditions on the structural, microstructural, and thermoelectric properties of the Cu<sub>11</sub>Mn<sub>1</sub>Sb<sub>4</sub>S<sub>13</sub> tetrahedrites was investigated. To continuing such works, we present some materials to be used as potential diffusion barriers for tetrahedrites. Carbon foil was selected for this study given the practical use of this material, being cheap, highly available, and easy to prepare. In our hot-pressing experiments graphite molds/crucibles are utilized to keep the tetrahedrite powders in place for densification. In other words, to allow the removal of the formed/dense pellet after the sintering process without damaging the graphite pistons, two carbon sheets/foils are used between the lower and upper pistons of the graphite mold. By keeping these two layers in contact with the tetrahedrite surface is possible to use them as diffusion barriers. This way, additional steps can be eliminated in the TE materials processing, which can help to the scale up materials production and accelerate the development and commercialization of based tetrahedrite TE

devices. Up to date, no works/studies have been made using carbon foil as an effective diffusion barrier in thermoelectric materials also including other copper sulfosalt families. Nevertheless, the high resistance to oxidation and thermal shock, chemical stability, and good electrical and thermal conductivity make this material very attractive for diffusion barrier experimentation [34]. Gold was selected given its high electrical conductivity and high resistance against oxidation [35]. For this material, there are no reports of being used/studied as diffusion barrier for TE generators using tetrahedrite based legs, however, it has already been used/studied on solar cells, bismuth-telluride based thermoelectric materials and other copper sulfosalts like the colusites [36]–[40]. On the referred studies, especially in Bi-Te materials, the diffusion of gold towards the interior of the samples was observed, resulting in material loss and contact degradation proportional to the tested temperatures [36], [37]. On colusites, in a study performed by Raju Chetty et al [38] a gold layer was joined into the TE material by hot-pressing. No secondary phases were observed at the interface between layer and substrate, with the layer been reported to adhere well to the substrate. However, long-term diffusion of gold into the colusite matrix was observed by SEM analysis conjugated with X-ray elemental mapping and XRD. This diffusion phenomena were letter proved to happen only during the hot-pressing experiments with no further diffusion being noticed after 48 h aging at temperatures close to 570 K.

### **EXPERIMENTAL DETAILS**

Cu<sub>11</sub>Mn<sub>1</sub>Sb<sub>4</sub>S<sub>13</sub> tetrahedrites were prepared by solid state synthesis using pure pieces of Cu (99.9999%, Alfa Aesar), Sb (99.9999%, Alfa Aesar), Mn (99.9%, Alfa Aesar), and S (99.5%, Alfa Aesar). The elements were weighted and mixed in stoichiometric ratios to achieve the proper composition. Each batch (~2 g) was sealed inside evacuated quartz ampoules  $(10^{-3} Pa)$  and heated from room temperature up to 1191 K, kept 1 h at this temperature and removed. To compensate the Sulphur losses during the synthesis processes, 0.6 % in weight of sulfur was added to each batch before the melting step. The obtained materials after melting were manually ground into powders, cold pressed (~512 MPa) and annealed at 723 K for 5 days. After annealing, the materials were ground again and hot-pressed at 848 K with 60 MPa for 90 minutes, resulting in dense pellets (< 90%) with ~10 mm diameter and ~3 mm height.

Carbon diffusion barriers were prepared along with the synthesis steps using carbon foils (thickness 0.5 mm, flexible graphite, 99.8% purity, Sigma-Aldrich) that were inserted on the top and bottom of the graphite molds/crucibles used for hot-pressing. Gold diffusion barriers were prepared by thermal evaporation using a *UNIVEX 300 Leybold Heraeus* evaporator. Pure gold pieces (99,999%, Sigma-Aldrich) were placed inside a molybdenum crucible that was heated to 1673 K by electrical current. Small pieces of tetrahedrite samples were mounted in aluminum masks located on the top of the deposition chamber (~16 cm above the gold). The pressure was set to  $1 \times 10^{-4}$  Pa and the gold was evaporated in few seconds. After prepared, the tetrahedrite materials with C and Au layers were sealed inside evacuated quartz tubes ( $10^{-3}$  Pa) and placed in a muffle oven at 648 K for 500 h.

X-ray diffraction (XRD) measurements were performed on a *Panalytical X'Pert PRO* diffractometer using a Bragg-Bretano geometry and a Cu K $\alpha$  radiation source. The tension was set to 45 kV and the current to 35 mA. The analysis of the hot-pressed materials was made by removing the carbon sheets, grinding them to powders and placing the particles on zero background Si single crystal sample holders. A similar procedure (remove of carbon and gold layers, grind to powders and place on zero background sample holders) was made for the samples with the diffusion barriers after aging. All data were acquired from 10° to 65° with a step size of 0.03° and 50 s of acquisition time. Diffractograms were processed using the *Origin* software and phase identification was performed by comparison with data from the

*Crystallography Open Database* (COD), the cell parameters of the hot-pressed Cu<sub>11</sub>Mn<sub>1</sub>Sb<sub>4</sub>S<sub>13</sub> tetrahedrite and the aged materials were calculated using *Powdercell* and *Unitcell* software's using the *Tim Holand and Simon Redfern* method [41].

Scanning electron microscopy (SEM), complemented with energy-dispersive X-ray spectroscopy (EDS), was used to study the microstructure and analyze semi-quantitatively the chemical composition of the hot-pressed and aged materials. Observations were made with an accelerating voltage of 25 kV using three different electronic microscopes: a) a JEOLJSM-7001F equipped with a field emission gun and an Oxford Instruments EDS system, b) *Philips XL 30 SFEG* equipped with a *Thermo Phisher EDS system*, and c) *Hitachi S2400* with *Bruker light elements EDS detector*. The materials for electronic microscopy observations were polished in wet conditions using ethanol (95%) and SiC sandpapers with P600, P1000, P1200 and P2000 grits.

To study the thermal stresses in the tetrahedrite substrates (and layers) during the aging treatments the COMSOL Multiphysics 5.5<sup>®</sup> program was used. The simulations consist of a 2D approximation model [42] that is based on a layered plate made of a tetrahedrite material (with  $7x3 \text{ mm}^2$ ) that is covered with gold or carbon layers with 0.5 mm in thickness. It must be noted that the used dimensions for the simulation models were selected based on our hot-pressing system capability, maximum sample length and thickness (~7x3 mm) and maximum layer thickness used (0.5 mm, like the carbon foil). The objective is to find the stresses due to CTE mismatch when the temperature of the materials increases from room temperature up to 648 K. For the simulations a Linear Elastic Material node and the thermal expansion attribute of the COMSOL® program were selected. These tools are based on Navier's equations and allow the calculation/computation of several parameters like the displacements, stresses, and strains. The simulations are based on the Finite Element Analysis theory (FEA) that uses adjusted meshes to solve general equations related to solid mechanics. For example, the linear elastic material node uses the general equation:  $-\nabla S = F_{\nu}$  (1), where  $F_{\nu}$  corresponds to the volume force,  $-\nabla$ . S to the divergence of stress, and S to the second Piola-Kirchhoff stress. At the same time, the thermal expansion node uses:  $\varepsilon_{th} = \alpha(T) (T - T_{ref})$  (2), where  $\varepsilon_{th}$  correspond the thermal strain,  $\alpha$  correspond to the coefficient of thermal expansion,  $T_{ref}$  to the initial temperature and *T* the input model temperature or final temperature.

To achieve convergence on the simulations, the Rigid Motion Suppression feature was added to the model builder window and a stationary study was made. The initial temperature of the models was set to 293 K and the input/final temperature set to 648 K. Material properties used in the equations for the gold layer like the density, thermal conductivity, heat capacity, Young modulus, and Poison's ratio were automatically computed from *COMSOL*<sup>®</sup> materials library. The CTE of gold was manually inserted on the program with that property being retrieved from F.C.Nix and D. MacNair work [43]. Material properties for the carbon layer were retrieved from the Gasket Materials web page, flexible graphite foil datasheet (properties across the thickness) [44], [45]. The mechanical properties of the tetrahedrite material were retrieved from other works that present the chemistry most close as possible to the Cu<sub>11</sub>Mn<sub>1</sub>Sb<sub>4</sub>S<sub>13</sub> composition [29], [32], [46]. For all the simulations, the meshes used to solve the presented equations were adjusted to a normal size.

Contact resistance measurements were made using a custom-made system based on a three-probe pulse measurement technique with a scanning probe integrated [47], [48]. The system consists in a micrometer positioning stage and a scanning probe, being the samples to measure fixed to a static base and connected to a nanovoltmeter and a current source (Keithley 2182A and Keithley 6220, respectively). For the measurements, both the nanovoltmeter and the current source were configured according to the delta mode (for low resistance) and were connected between each other and the sample for data processing. A current of 2 mA and pulses of 1 ms between the current source and the nanovoltmeter were used. The sample was scanned

with a 100  $\mu$ m step between measurements and the objective of the pulses is to minimize the thermoelectric tensions like the Peltier effect. To perform the contact resistance measurements, a tetrahedrite sample with a carbon diffusion barrier was cut in ~7x3.5 mm dimension and glued to ~0.5 mm copper contacts using silver conductive varnish. To obtain a good electrical contact a constant pressure of ~ 60 MPa was used, and the sample was left to dry (under pressure) at room temperature during 24h.

### **RESULTS AND DISCUSSION**

A typical XRD diffractogram of the original hot-pressed material is presented in Fig. 1. The sample is mainly constituted by the tetrahedrite cubic phase, space group I-43m (COD card #8140303), with no signs of other compounds. Moreover, for higher 20 values a doublet splitting caused by  $k_{\alpha 2}$  radiation can be observed, which indicates a high crystallinity and low defects concentration in the material. Figure 2 shows a micrograph of a polished surface of the same sample (hot-pressed Cu<sub>11</sub>Mn<sub>1</sub>Sb<sub>4</sub>S<sub>13</sub>) being possible to observe a homogenous matrix with low porosity, but minor amounts of secondary phases are also present. These secondary phases could not be detected by XRD given their low concentration. EDS semi-quantitative analysis of the phases compositions is summarized in Table 1. According to the results, the matrix corresponds to the Cu<sub>11</sub>Mn<sub>1</sub>Sb<sub>4</sub>S<sub>13</sub> tetrahedrite compound, confirming the XRD results, while the secondary phases are identified as chalcostibite (CuSbS<sub>2</sub>). Some differences between the nominal and practical tetrahedrite composition can be observed as well, still, they are within the experimental error. The presence of chalcostibite in manganese doped tetrahedrites was also previously reported by Wang et al. [31], where similar synthesis routes, based on solid state reactions, with melting, annealing for long periods (2 weeks), and hot-pressing steps, were adopted. For the hot-pressing experiments these authors used a pressure of 723 K and 70 MPa for 30 min, while in the present work higher temperatures and sintering times were used.



Fig. 1. XRD diffractogram of the hot-pressed Cu<sub>11</sub>Mn<sub>1</sub>Sb<sub>4</sub>S<sub>13</sub> material (top) and tetrahedrite pattern simulation using data from the *Crystallographic Open Database* (bottom).



Fig. 2. SEM micrography of the hot-pressed  $Cu_{11}Mn_1Sb_4S_{13}$  material, with a magnification of 50 X. Analysis in back scattered electrons mode (BSE). Secondary phases detected by EDS are indicated by arrows.

Table 1. EDS results for phases identified in the hot-pressed  $Cu_{11}Mn_1Sb_4S_{13}$  sample with the sum of all atoms in the formulas normalized to 29 and 4 for the tetrahedrite and chalcostibite phases respectively.

	Composition at %.				_	
Sample	Cu	Mn	Sb	S	Phase	Normalized compositions
Hot-	27(3)		26(3)	47(6)	CuSbS <sub>2</sub>	$Cu_{1.1(0.1)}Sb_{1.0(0.1)}S_{1.9(0.2)}$
pressed	37(4)	4(1)	16(2)	43(5)	$Cu_{11}Mn_1Sb_4S_{13}$	$Cu_{10.7(1.3)}Mn_{1.2(0.1)}Sb_{4.6(0.6)}S_{12.5(1.5)}$

The XRD diffractograms of the Cu<sub>11</sub>Mn<sub>1</sub>Sb<sub>4</sub>S<sub>13</sub> substrates covered with gold and carbon layers and aged at 648 K for 500 h are shown on Figure 3. Like in the original (unaged) material, also here only a tetrahedrite phase is detected and no signs of secondary phases were found. Being also possible to observe some doublet splitting that is caused by  $k_{\alpha 2}$  radiation. The absence of secondary phases suggests that no significant reactions between the tetrahedrite and the layers occurred and that both materials can be used as diffusion barriers. To confirm this possibility and better understand the nature of the tetrahedrite/layers interface, SEM observations were performed. In the aged materials (Figure 4) it is possible to identify a porous matrix, that can be ascribed to tetrahedrite, and the layers, without traces of any other phases. The porosity is slightly higher than in the hot-pressed (unaged) material (Figure 1), which can be related to the releasing of tensions during the aging treatment [49] and to sulfur evaporation/sublimation over time. Some white spots can be seen in figure 4 c) and d) which correspond to oxidized particles/debris resultant from sample polishing.



Fig. 3. XRD diffractogram of the Cu<sub>11</sub>Mn<sub>1</sub>Sb<sub>4</sub>S<sub>13</sub> samples aged with Au and C layers during 500 h at 648 K under vacuum conditions. Tetrahedrite pattern simulation on the bottom, using data from the COD.

The gold layer (white zones in Figure 4 b) is thin, with less than 10  $\mu$ m thickness, and some discontinuous zones are observed. It is worth to mention that the samples were polished

before SEM observations and that small portions of the Au coating stayed stuck to the forceps tips, pointing to an insufficient adhesion. In fact, during the polishing process small gold pieces were released from the sample and have folded in the interface area (edge of the sample), being still possible to observe some parts at the SEM micrography right top (Figure 4 b). The releasing/detachment of the layer is most probably induced by the smoothness of the tetrahedrite surface where the gold was deposited (a less irregular surface has less area exposed for deposition and the adhesion is reduced). For the future, more tests must be done in this regard, specially to improve the adhesion of gold to the tetrahedrite substrate.

One way to solve the adhesion problem could be the increase of the tetrahedrite surface roughness [50], by polishing with bigger grits sandpaper, chemical etching, or using other methods. The reduction of the thickness of the Au layer could be considered as well, having into account other works where smaller thicknesses (of gold or other material layers) adhere well to tetrahedrite substrates and other Cu Sulfosalts surfaces [27], [39], [40]. For example, S. Battiston et all [27] while studying AlTiN based thin films for protection against degradation of Ni-Zn doped tetrahedrites reported a bad adhesion between the coatings and the tetrahedrite materials for layers deposited by DC magnetron sputtering that presented thicknesses bigger than 2.6 µm. To solve the adhesion problem, the authors decided to deposit thinner coatings with 450 nm of thickness. In the same work, the authors highlighted that the main reason for the coatings bad adhesion was related to a thermal-mechanical incompatibility between the coatings and substrates, with the coefficients of thermal expansion for each material being very different, i.e.  $\sim 7.5 \times 10^{-6}$  K<sup>-1</sup> for the AlTiN coatings and  $\sim 15 \times 10^{-6}$  K<sup>-1</sup> for the tetrahedrites (in a 293 to 673 K temperature range). In our work, that should not be the case for the Au layer, given the fact that Cu<sub>11</sub>Mn<sub>1</sub>Sb<sub>4</sub>S<sub>13</sub> tetrahedrites and gold should have closer coefficients of thermal expansion,  $\sim 14 \times 10^{-6} \text{ K}^{-1}$  and  $\sim 13.5 \times 10^{-6} \text{ K}^{-1}$  respectively (at temperatures close to 670 K [43], [46]). Another example of the effectiveness of gold layers can be found in the work of Yueli Liu et all [39] which have studied Cu<sub>12</sub>Sb<sub>4</sub>S<sub>13</sub> quantum dots as efficient inorganic hole transport materials for solar cells. In the referred work, an Au layer was deposited by thermal evaporation on the top of a tetrahedrite substrate. The authors didn't specify the thermal evaporation conditions but a continuous and homogeneous Au layer with a thickness of 80 nm was obtained. Although no information is provided about the adhesion of the gold layer, a clean interface between coating and substrate can be observed, without being noticed the presence of cracks or detachments on the SEM micrograph presented in the work. Similar results were obtained for other copper sulfosalts like the chalcostibites (CuSbS<sub>2</sub>), were in the work of Yafeng Xu et all [40], a gold layer with a thickness of 60 nm was deposited by thermal evaporation under a CuSbS<sub>2</sub> substrate. Through SEM observations, the formation of secondary intermetallic phases or layer detachments were not observed. In summary and according to all the studies presented, the formation of secondary phases that lead to layer detachments or the appearance of cracks at the tetrahedrites substrates is unlikely when gold layers are deposited, which reinforces that Au can in fact be used as an effective diffusion barrier for tetrahedrites or other Cu sulfosalt materials.

The EDS semi-quantitative analysis displayed at Table 2, presents results of the gold layer and tetrahedrite matrix after aging. No secondary phases were detected, with the disappearance of chalcostibite and the increasing of the copper amount in the tetrahedrite matrix suggesting the sulfur evaporation/sublimation. This phenomenon was already verified on previous works [33] and implies the increasing of the copper concentration on the tetrahedrite matrix as sulfur evaporates over time.



Fig. 4. SEM Micrography's of Cu<sub>11</sub>Mn<sub>1</sub>Sb<sub>4</sub>S<sub>13</sub> samples with gold (a,b) and carbon layers (c,d) after aging during 500 h at 648 K under vacuum atmosphere. Micrography's a) – 100 X, and b) – 500 X magnification in BSE mode, and c) – 150 X, and d) – 1500 X on Secondary Electrons mode (SE). Numbers correspond to EDS analysed zones – see Table 2.

Table 2. EDS semi-quantitative analysis results for phases in the hot-pressed  $Cu_{11}Mn_1Sb_4S_{13}$ sample with gold and carbon layers after ageing at 648 K for 500 h and with the sum of all atoms of the tetrahedrite formula normalized to 29.

			Compos	ition at.	%			
Zone	Phase Type	Cu	Mn	Sb	Au	С	S	Normalized compositions
1-Au <sub>a</sub>	CuAu	40(10)			60(10)			$Cu_{0.8(0.1)}Au_{1.2(0.1)}$
2- Tetra <sub>b</sub>	$Cu_{12}Sb_4S_{13}$	40(5)	3(1)	14(2)			43(5)	$Cu_{11.6(1.4)}Mn_{0.9(0.1)}Sb_{4.1(0.5)}S\\_{12.5(1.5)}$
<b>3-C</b> <sub>c</sub>						100 (12)		
4- Tetra <sub>e</sub>	$Cu_{12}Sb_4S_{13}$	46(6)	4(1)	14(2)			36(4)	$Cu_{13.3(1.6)}Mn_{1.2(0.1)}Sb_{4.1(0.5)}S\\_{10.4(1.3)}$

a. Gold layer; b. Tetrahedrite matrix; c. Carbon layer; e. Tetrahedrite matrix.

At the same time, a substantial concentration of Cu was revealed in the Au layer (Table 2, 1-Au), which can be explained by the extended and easy solubility between gold and copper and by the small thickness of the gold layer and the Cu diffusion from the tetrahedrite phase. Significant Cu diffusion rates can exist on tetrahedrite samples with copper excess [51], a situation easily established by the sulfur evaporation/sublimation. However, only minor stoichiometry changes in the tetrahedrite matrix are observed (Table 2, 2-Tetra). When comparing the unaged (hot-pressed) material with the aged one, is also possible to observe an

increase in the copper amount from 37% to 40%, suggesting that the copper excess migrated to the gold layer, which can act not only as an effective diffusion barrier for tetrahedrites, but also as a composition buffer by maintaining the Cu-S balance in the tetrahedrite matrix and keeping the tetrahedrite stoichiometry. According to the Cu-Au phase diagram [52], as copper diffuses towards the gold layer some Cu-Au alloys must be formed, which confirms the presented ideas.

Comparable results using gold layers on colusite TE materials were described by Chetty et al [38]. In that work, no secondary phases were formed between the TE material and Au layer, but a significant solubility of Nb in Au was detected. The authors also reported that the use of a gold diffusion barrier at the TE joints reduced the specific contact resistance, being obtained a resistivity of ~19  $\mu\Omega$  m comparatively with the one obtained for the same material using just copper contacts (~30  $\mu\Omega$  m). These low resistivity values increased the performance of the colusite based TE legs, which resulted in an energy conversion efficiency upgrade of about 3.3%. It is worth to mention that for the contact resistance measurements the authors prepared a ~5 mm colusite sample with copper/Ag and Sn<sub>60</sub>Pb<sub>40</sub> contacts in which the electric contacts had at least 1.3 mm, where the gold layer had about ~300  $\mu$ m with the joints being prepared by hot-pressing and without the use of any paint or solder.

In the sample with carbon layer (Fig. 4 c and d), a continuous and thick coating (~ 400  $\mu$ m) with good adhesion to the tetrahedrite phase being observed. Such layer is only composed by carbon, as indicated by the EDS analysis (Table 2, 3-C). However, a change in the composition of the aged tetrahedrite matrix can be observed, when compared with the non-aged material (Table 2, 4-Tetra). At the same time it can be noticed an increase in the copper amount (from 37 at.% to 46 at.%) and a decrease in sulfur (from 43 at.% to 36 at.%), which is probably related to sulfur evaporation/sublimation from the tetrahedrite surface during the aging treatments, similarly to what was suggested for the gold layer sample. However, in this case a stoichiometry balance can't be maintained, as sulfur sublimation takes place the copper rises in concentration on the tetrahedrite matrix affecting the stoichiometry of the material as can be seen in Table 2, 4-Tetra. This assumption is again corroborated by the disappearance of the minor amounts of the chalcostibite (sulfur-rich) phase previously observed in the hot-pressed material. No secondary phases were detected at the interface between the tetrahedrite material and graphite layer, which points to the successful use of graphite layers as diffusion barriers.

The mesh parameters calculated from the DRX data for each sample (figures 1 and 3) are presented in Table 3. The values obtained are in the range of the ones presented in the literature for manganese doped tetrahedrites, between 10.3700 - 10.4200 Å [53], [54]. Comparatively to the original and unaged material, the aged tetrahedrite with the gold layer present the higher mesh parameters. These values reinforce the hypothesis of copper diffusion towards the gold layer as presented above, since the increase of the mesh parameters can be explained having in consideration that Cu atoms must exist in the tetrahedrite structure in different oxidation states (1 + and + 2) while occupying the 12d and 12e sites. When the material is left to age, at 648 K during 500 h, copper diffusion towards the gold layer is observed, if the copper atoms that diffuse are in the 2+ oxidation state, their migration can result in an increase of the tetrahedrite mesh parameters due to rearrangements of the less oxidized and bigger copper and manganese species like the  $Cu^{+1}$  and  $Mn^{2+}$  that occupy the 12d crystallographic sites and are bigger than the  $Cu^{2+}$  ions. On the other hand, on the tetrahedrite with the carbon layer is possible to observe a contrary effect with the decrease of the mesh parameters when comparing to the unaged material. Again, this decrease can be explained by the oxidation of the Cu atoms over time. As the material ages it becomes more oxidized and more Cu<sup>2+</sup> ions should be present at the tetrahedrite structure which consequently causes a reduction of the mesh parameters.

Table 3. Lattice parameter a for the Cu<sub>11</sub>Mn<sub>1</sub>Sb<sub>4</sub>S<sub>13</sub> samples, unaged, and aged 500 h under vacuum conditions at 648 K with Au and C layers.

Sample	Cell parameter a (Å)
Hot Pressed Cu <sub>11</sub> Mn <sub>1</sub> Sb <sub>4</sub> S <sub>13</sub>	10.3771 +/- 0.0003
Cu11Mn1Sb4S13 with Au layer	10.3822 +/- 0.0003
Cu <sub>11</sub> Mn <sub>1</sub> Sb <sub>4</sub> S <sub>13</sub> with C layer	10.3755 +/- 0.0003

A similar relation for the lattice parameters was made by Chetty et ell [55], while studying the thermoelectric properties of Co substituted tetrahedrites. In such work, the authors noticed an increase in the lattice parameters as the doping content of Co increases. This effect was contradictory to the predictions, since it was expected that the substitution of copper by cobalt on the tetrahedrite matrix should lead to smaller mesh parameters, since the Co atoms have a smaller radius than the Cu species. However, it was observed by the authors that upon doping a partial substitution of the  $Cu^{2+}$  (0.0057 nm) species by the larger ionic radios  $Co^{2+}$  (0.0058 nm) have taken place, which leaded to an increase of the mesh parameters contrary to what was expected. To finish, it's important to say that this effect is common on tetrahedrite materials and explains why there are such ranges in the mesh parameters reported across the literature.

To better study if the C and Au layers can be used as effective diffusion barriers for tetrahedrites, several simulations were made using the *COMSOL Muliphisics*<sup>®</sup> program. The simulation of the thermal stresses in a tetrahedrite material covered with a gold layer is presented in Fig. 5. For clarity, the results presented in figure 5 are the normal stresses in the x direction that are represented on a deformed configuration caused by thermal expansion, with exaggerated displacements for a clear view.

As both materials (gold and the tetrahedrites) have similar coefficients of thermal expansion [43], [46], the thermal stresses presented on the simulations are relatively low. However, the gold layer presents a slightly higher CTE than the tetrahedrite material, which makes the gold to expand more than the tetrahedrite substrate at 648 K, causing tensile stresses at the interface between both and placing the gold layer under compression. This effect can lead to the appearance of cracks at the tetrahedrite substrate or to coating detachments due to contraction and expansion of the materials (blistering) [56]. However, no cracks were observed between the tetrahedrite and the gold (figure 4 - a) and b)) in our experiments, nevertheless the compression stresses observed in the simulation could be one possible cause for the weak adhesion observed for the gold layer in our study.

The Simulation of thermal stress of a tetrahedrite substrate covered by a graphite layer can be observed in Fig. 6. This second case is very similar to the first one, as the graphite layer has a higher CTE than the tetrahedrite, the layer wants to expand more and suffers compression while the interface becomes under tension. Still, the stresses in this case are smaller than the ones calculated on the gold layer simulation ( $\sim$ 15/-25 MPa comparing to  $\sim$ 8/-4 MPa). This difference can be explained due to the softness of the graphite layer (low Young modulus), which gives the material the ability to act as a mechanical buffer.

In general, the simulations agree with the results observed through electronic microscopy where crack free interfaces can be observed, meaning that the stresses at the interface between the layers and substrates must be low, however, more tests must be done in the future, being important to perform measurements of the CTE of the  $Cu_{11}Mn_1Sb_4S_{13}$  tetrahedrites for more accurate simulations.



Fig. 5. Normal stress in x direction of a tetrahedrite material covered with a gold layer and heated from room temperature up to 648 K.



Fig. 6. Normal stress in x direction of a tetrahedrite material covered with a graphite layer and heated from room temperature up to 648 K.

Contact resistance measurements of the tetrahedrite sample prepared with a carbon diffusion barrier and copper contacts are presented in Fig. 7. Since the gold layer still needs to be optimized (due to the bad adhesion observed) and, at the same time, increasing its thickness by layer preparation *via* hot pressing is not an option in the scope of our work (which pretends to develop cheap TE generators), we decided to dedicate the subjects regarding the gold layer to a future and separated work.



Fig. 7. Contact resistance measurements of a Cu<sub>11</sub>Mn<sub>1</sub>Sb<sub>4</sub>S<sub>13</sub> tetrahedrite prepared with a carbon diffusion barrier and a copper electrical contact, a) measurement schematization, and b) results obtained by sample scanning.

According to the results presented in figure 7, a resistance jump of about ~34 m $\Omega$  mm<sup>2</sup> can be observed when the resistance probe passes from the tetrahedrite material to the copper contact. On the figure, it is possible to observe a resistance increase as the distance from the copper contact increases, which is a typical plot from a resistance contact measurement between a metal and a semiconductor material [48], [57]. The value observed in this jump should contemplate the resistance between the tetrahedrite material, the carbon layer, and the silver conductive paint used to connect to the copper contact. This implies that the resistance between the tetrahedrite substrate and the carbon diffusion barrier should be lower than the registered/observed value. Its also important to mention that the measured results are in the range of other commercial materials like the TEG's based in BiTe (~0.075 to 3.7 m $\Omega$  mm<sup>2</sup> [38],[47], [57]). However, when directly comparing with the results presented in such ways, the measured contact resistance values are from ~10 to 450 times higher. These differences can be explained by several aspects like the TE materials used, the materials used for the diffusion

barriers and electrical contacts (Cu, Al etc), and the techniques to build/connect the electrical contacts. For example, in Chetty's work [38] the electrical contacts were prepared by hotpressing and without the use of any paint or solders, while in our case a cold pressing method and a conductive silver paint was used. This latter methodology used for the preparation of the electrical contacts could lead to a smaller bonding strength between the tetrahedrite matrix and the copper which reduces the quality of the electric contacts. Another very important aspect to have in consideration is related to the fact that for the case of tetrahedrites, there are still no reports/studies on solders or conductive paints to be used for jointing fabrication, meaning that there are still plenty of room for optimization of the electric contacts quality. For future works is extremely important to identify optimum solders and paints that can be used for jointing fabrication and identify as well which techniques (cold pressing, hot-pressing, thermal spray, thermal evaporation, etc.) are the best for design optimal contact interfaces. Since the contact resistance at the TE joints can be a critical point affecting the devices performance more tests must be done in this regard.

#### CONCLUSION

Gold and carbon layers were tested as diffusion barriers for  $Cu_{11}M_1Sb_4S_{13}$  tetrahedrites, with the materials being exposed to 648 K during 500 h under vacuum conditions. The absence of secondary phases suggests that both layers can be used as effective diffusion barriers. However, a significant copper concentration was detected in the gold layer, pointing to its diffusion from the tetrahedrite and suggesting an excess of this element in the matrix phase, probably due to sulfur sublimation. Despite these facts, only minor changes were found in the stoichiometry of the aged tetrahedrite comparatively with the non-aged material, suggesting that the gold layer acts as a composition buffer. An excess of the copper amount and a decrease in sulfur is also found on the tetrahedrite matrix of the sample with the carbon layer, reinforcing the hypothesis of sulfur sublimation during the aging tests. Film discontinuities are observed in the tetrahedrite surface. On the other hand, crack free interfaces were observed for both layers, indicating a good match among the coefficients of thermal expansion that agree well with the simulations made using the *COMSOL*<sup>®</sup> program, where low stresses can be observed at the interface between the materials (substrate and layers).

To the Authors best knowledge, this is the first study on diffusion barriers for thermoelectric tetrahedrites reported until now. However, it is fundamental to make new studies on the search of novel materials for effective diffusion barriers for sulfide compounds, as tetrahedrites. Only with efficient diffusion barriers will be possible to develop TE modules suitable for commercial applications, as the reactivity and vapor pressure of the thermoelectric material constituents, particularly of sulfur, possess hard challenges to avoid chemical reactions and, consequently, the degradation of the materials.

Contact resistance measurement between the tetrahedrite material and a copper contact display a low value, within the order of other commercial devices, which points to the successful use of carbon as an effective diffusion barrier. Yet, more study's need to be done to find an optimal method for junction fabrication, another very important aspect that affects the performance of TEG's.

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# A STUDY OF ELECTROCHEMICAL DISSOLUTION OF PLATINUM

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### ABSTRACT

Platinum is one of the most studied metals in electrochemistry because it has excellent anticorrosive properties. Platinum recovery is important due to its extremely limited availability, vast industrial applications and high market demand. Platinum recycling can be made through traditional methods or electrochemical methods. Traditional methods have a negative impact on the environment because they involve the use of a huge amount of acids at high concentrations and the use of energy-intensive equipment. The electrochemical methods are less harmful to the environment and can achieve high recovery efficiency. In this work, dissolution of platinum was studied in different parameter changes, such as electrolyte solutions, electrochemical methods, scan rates, time etc. We target the fundamental understanding of platinum recycling rather than it characterization. A platinum disk electrode with a geometrical area of 0.785 cm<sup>2</sup> was used in this work as a working electrode. After experimenting with this electrode, we developed an electrochemical protocol for recycling platinum from used catalytic converters. All resulting solutions were analysed by ICP – OES technique to determine the amount of platinum diskolved.

Keywords: platinum, dissolution, recycling, electrochemistry, catalytic converters

### **INTRODUCTION**

Platinum is the most used metal in electrochemistry due to its physical and chemical properties [1]. Its main uses are in the automotive industry as a catalyst to reduce pollution and in the chemical industry. To reduce the catalyst loading in catalytic converters, the platinum and palladium nanoparticles (<20 nm) are deposited on a honeycomb ceramic support (i.e. cordierite). The role of precious metals in catalytic converters is to oxidize and reduce various toxic gases. Platinum is part of the platinum metal group (PGM), together with palladium, rhodium, ruthenium, osmium, and iridium [2, 3]. The natural resources of these metals are increasingly limited, being found only in South Africa, Russia, Canada, and North America [3].

Currently, a few methods for platinum recovery are used, but most of them have various disadvantages [4]. PGM extraction methods can be classified into three groups: pyrometallurgical, hydrometallurgical and electrochemical. The pyrometallurgical methods need a higher quantity of energy and special equipment in order to reach the required temperatures, while the hydrometallurgical processes are harmful for the environment. Due to the high recovery rates, pyrometallurgical recovery methods are favoured for the recycling of platinum metals. Pure platinum is generally obtained using hydrometallurgical methods [5].

Lately, scientists and specialists from the industry have started focusing on electrochemical methods [6], where the PGMs from car catalysts are dissolved in chlorine, such as HCl or KCl. Several electrochemical methods and parameters used for platinum recovery are presented in this article.

According to the literature, platinum is best solubilized in an acid solution. The Pourbaix diagram or potential-pH diagram, shows that platinum in its metallic form dissolves into  $Pt^{2+}$  platinum ions during anodic polarization in a strongly acidic environment (pH <0) [7]. In the presence of Cl-, Pt forms bonds with this ion and can be found in the solution as the [PtCl<sub>4</sub>]<sup>2-</sup> or [PtCl<sub>6</sub>]<sup>2-</sup> complex. [8, 9]

## METHODOLOGY

The experimental setup consisted of a three-electrode setup connected to a potentiostat (OrigaFlex – OGF500). The potentiostat was controlled by a computer with a specific software (OrigaView). As working electrodes, we used a polycrystalline platinum electrode, glassy carbon with Pt/C and titanium plates for a catalytic converter. For reference, we've used calomel (Hg/Hg<sub>2</sub>Cl<sub>2</sub>), Hg/Hg<sub>2</sub>SO<sub>4</sub> or Ag/AgCl electrodes and a graphite rod as the auxiliary electrode. Ag/AgCl was used for experiments where electrochemical methods were tested. Hg/Hg<sub>2</sub>Cl<sub>2</sub> was used only for experiments with chloride-containing electrolytes and Hg/Hg<sub>2</sub>SO<sub>4</sub> was used for experiments with chloride to avoid contamination with chloride from Hg/Hg<sub>2</sub>Cl<sub>2</sub> electrode. The potentials were converted to reversible hydrogen electrode (RHE) using the following equation:

 $E(RHE) = E_{ref} + 0.059 \text{ pH} + E_{\circ_{ref}}$ , where  $E_{ref}$  is working potential from these studies and  $E_{\circ_{ref}}$  is the standard potential or our reference electrodes at 25 °C.

The first experiments were performed in different pH solutions. Two of them had a strong acidic pH (1M HCl and 0.5 M  $H_2SO_4$ ) and two of them had neutral pH (1M KCl and 0.5 M  $K_2SO_4$ ). Measurements were performed at 25°C. Spent catalytic converters were supplied from a local shop. ICP – OES (Perkin Elmer) was used in order to determine the amount of platinum dissolved. The calibration curve was plotted using the Multi-Element Calibration Standard 4. UV – VIS technique (Jasco V – 550) was used to identify the chemical structure of the platinum compounds.

# **RESULTS AND DISCUSSION**

### Effect of electrolyte solutions on platinum dissolution

Fig. 1 shows the cyclic voltammograms for the first set of experiments, where we tested four electrolyte solutions. Two of them had a strong acid pH (Fig. 1A) and two were with a pH around 7 (Fig. 1B). The hydrogen region was found in acidic electrolytes (Fig. 1A) at potentials from -0.1 to 0.3 V vs. RHE. Platinum oxidation onsets at 0.85 V vs. RHE and 1.1 V vs. RHE for sulphuric acid and hydrochloric acid, respectively. On the negative sweep, the peaks at 0.75 V vs. RHE and 1.25 V vs. RHE correspond to platinum oxide reduction in sulphuric acid and hydrochloric acid, respectively. Oxygen and chlorine evolution starts at 1.3 V vs. RHE in 1 M HCl. Oxygen evolution in 0.5 M H<sub>2</sub>SO<sub>4</sub> onsets at 1.6 V vs. RHE. Fig. 1B shows the Pt cyclic voltammograms (CVs) at neutral pH. The hydrogen region in 1 M KCl was found between -0.3 and 0.6 V vs. RHE. In the case of 0.5 M K<sub>2</sub>SO<sub>4</sub>, the hydrogen region was found between -0.2 and 0.3 V vs. RHE. Platinum oxidation starts at 1.0 V vs. RHE and 1.3 V vs. RHE in 0.5 M K<sub>2</sub>SO<sub>4</sub> and 1 M KCl, respectively. The platinum oxide reduction showed two peaks at 0.5 V and 1.0 V vs. RHE on the cathodic sweep (i.e. negative currents) in 0.5 M K<sub>2</sub>SO<sub>4</sub>. Platinum oxide reduction showed one peak at 1.1 V vs. RHE on 1 M KCl.

Oxygen and chlorine evolution starts at 1.5 V vs. RHE in 1 M KCl. Oxygen evolution in 0.5 M  $K_2SO_4$  onsets at 1.7 V vs. RHE.



Fig. 1. CVs recorded with polycrytalline platinum disk electrode at 0.1 V/s A) acidic electrolytes; B) neutral electrolytes

Oxygen evolution onsets at smaller potentials in chloride-containing electrolytes than sulfate-containing electrolytes. Such a negative shift in potential can be reasoned on the basis of mixed oxygen/chlorine evolution. The current density in chloride-containing electrolytes was significantly larger than in sulfate-containing electrolytes. The reader should bear in mind that the chlorine evolution is the faster 2-electron reaction as opposed to the 4-electron oxygen evolution reaction. Platinum oxide reduction showed two peaks (red curve in Fig. 1B). Such a behaviour can be explained by the reduction of oxygen with protons and hydroxides that usually takes place at neutral pH [10]. Hydrogen evolution takes place at negative potentials in electrolyte solutions with neutral pH which is well-known according to the literature [9, 11].

Fig. 2 shows the results of elemental analysis for each electrolyte solutions. The results from ICP – OES show that the best dissolution of Pt is achieved in HCl (approx. 2.5mg/L), followed by KCl (0.3mg/L) and H<sub>2</sub>SO<sub>4</sub> (0.06mg/L). Pt dissolution in K<sub>2</sub>SO<sub>4</sub> was below the detection limit (i.e. 0.01 mg/L), however, Pt dissolution cannot be fully excluded. The largest dissolution was achieved in chloride-containing electrolytes which underlines the importance of chloride. There was a 2-fold improvement in the platinum dissolution in electrolytes that contain chlorine as opposed to sulfate-containing electrolytes. Such finding emphasizes that chlorides are more important than protons in the Pt dissolution. It is well known that the electrochemical dissolution of Pt in chloride-containing electrolytes leads to the formation of water-soluble [PtCl<sub>6</sub>]<sup>2-</sup> [9, 12]. Another set of experiments for this study was platinum dissolution comparison between three electrochemical methods: cyclic voltammetry, potential hold, and potential step (Fig. 4). The electrolyte solution for this experiment was chosen from previous experiments.



Fig. 2. Quantity of dissolved platinum during pH experiments

Effect of electrochemical methods on platinum dissolution



Fig. 3. Electrochemical setup with polycrystalline platinum electrode

The experiments were performed in 1M HCl for 24 hours. The lower potential limit (LPL) and upper potential limit (UPL) were 0.45 V vs. SHE and 1.25 V vs. SHE, respectively. The platinum dissolution rate was 2.014 mg/L, 8.607 mg/L and 0.01 mg/L for cyclic voltammetry, potential step (PS) and potential hold (PH), respectively (Fig. 4 and Table 1). In the case of step potential, the step is varied between the lower potential limit and the upper potential limit. The potential was applied for  $\tau = 3s$  for the total period of t = 24h. Platinum dissolution is enhanced when oxidation and reduction reactions take place. If the maximum potential is constant, it means that the Pt surface is oxidized or chlorinated. If Pt is oxidized or chlorinated, then Pt is no longer active from an electrochemical point of view and ions can't be released in the solution. Pt dissolution rate (Table 1) was calculated by dividing the amount of dissolved Pt by the geometric area of the electrode and normalized to the time. Table 1 showed that the platinum dissolution trend was: PS>CV>>PH. A similar Pt dissolution rate was achieved for the PH irrespective of the applied potential.



Fig. 4. Amount of dissolved Pt during 24 hours for each electrochemical method



Fig. 5. Electrochemical setup for Pt/C deposed on glassy carbon electrode

	UPL (V vs.	LPL (V vs.	Dissolution rate ( $\mu g^{*}h^{+}cm^{-}$
	SHE)	SHE)	<sup>2</sup> geo)
CV: v = 0.1V/sec	1.25	0.45	20.8
PS: $\tau = 3$ sec; t =	1.25	0.45	81.9
24h			
PH: t = 24h	1.25	-	0.1
PH: t = 24h	-	0.45	0.1

Table 1. The parameters and results of electrochemical methods

UPL – upper potential limit; LPL – lower potential limit

### From polycrystalline Pt to nanoparticles

In previous experiments, we showed that polycrystalline platinum is susceptible to electrochemical dissolution. It is well known that Pt is more electrochemically active in nanoparticle form which means that it can be easily dissolved. To validate the PS method, the electrochemical setup presented in Fig. 3 was adapted to Fig. 5. Fig. 5 shows the electrochemical setup, the bare glassy carbon (GC) and Pt/C covered GC. The transmission electron microscopy (TEM) showed Pt nanoparticles (black circles) deposited on active carbon (light grey). Pt nanoparticles with less than 5 nm were found on the carbon surface. Energy dispersive X-ray (EDX) spectrometry revealed the presence of carbon, platinum and copper. Pt/C was deposited on Cu grids which explains the Cu presence in the EDX.

Table 2 shows the results for two experiments with Pt/C covered GC. The experiments lasted 15 and 60 seconds. Electrodes were covered with approx. 54  $\mu$ g Pt/C catalyst. The platinum dissolution was 23.6  $\mu$ g and 51  $\mu$ g for 15 and 60 seconds, respectively. It means an efficiency of 43% and 93% for 15 and 60 seconds, respectively. The platinum dissolution rate was calculated by dividing the mass of the electrode catalyst to the geometrical surface of the electrode normalized to the time. Table 2 shows that 60 seconds are enough to dissolve almost all Pt nanoparticles.

Time of experiment (PS)	Pt/C Catalyst deposited on the electrode (µg)	Platinum dissolution in 20 mL (µg)	Efficiency (%)	Dissolution rate (mg / cm <sup>2</sup> *h)
15 seconds	54.7	23.6	43	11.33
60 seconds	54.7	51	93.2	6.12

Table 2. Results for Pt/C experiments which lasted 15 and 60 seconds

Fig. 6 shows the working electrode manufacturing procedure with the spent catalytic converter. The TEM investigation of the catalytic converter shows two types of nanoparticles (red and green circles). The nanoparticles were deposited on a light grey support. EDX shows the presence of Mg, Al, Si, Pt, Pd and Cu. The catalytic converter used in this experiment contained 394 mg/kg palladium and 133 mg/kg platinum, which means approx. 0.046% Pd and 0.014% Pt.

Fig. 7 shows the TEM investigation of the catalytic converter at the nanoscale. Dark-black circles are kept in place by a light grey support. Metallic nanoparticles were identified based on their crystallographic interplanar distance, which is 2.25 Å and 1.96 Å for Pd (Fig. 7A) and Pt (Fig. 7B), respectively.



Fig. 6. TEM for catalytic converter used in this study

The support of choice in automotive catalytic converters is cordierite. Cordierite is a magnesium doped aluminium-silicon mixed oxide. The signal of Mg, Al and Si in EDX confirms the presence of cordierite. The contrast in TEM is given by the electron density of the element. Therefore, elements with a higher electron density, such as Pt and Pd, are darker. Elements with a lower electron density have a light grey color. It can be inferred that Pt and Pd are deposited on the cordierite surface, similar to Pt deposited on carbon.

Table 3 shows the results for two types of experiments with catalytic converter. The chronoamperometry method with the potential step was used for both experiments. The potential values were identical to the previous experiments. Table 3 reports the values for an experiment in which a sonotrode was introduced, called sonoelectrochemistry experiment. The mass of Pt on the electrode was 3.77  $\mu$ g Pt and 2.39  $\mu$ g Pt for the conventional and sonoelectrochemical experiments, respectively. The Pd mass on the electrode was 11.14  $\mu$ g Pd and 7.08  $\mu$ g Pd for the conventional and sonoelectrochemical experiments, respectively. The conventional electrochemistry efficiency was 13 % and 14 % for Pt and Pd, respectively. The sonoelectrochemistry efficiency was 35% and 28 % for Pt and Pd, respectively. The sonoelectrochemistry experiment doubled the efficiency. It means that the sonoelectrochemistry improves the electrode kinetics and diffusion processes from the electrode-electrolyte surface. To demonstrate that the sonoelectrochemistry can improve the platinum dissolution, the experiments were made with the setup from Fig. 3.

The results for the sonoelectrochemistry experiment versus the conventional method are presented in Fig. 8. The conventional method was an experiment with simple chronoamperometry–potential step. On the x axis is the time for each experiment in minutes (30, 60, 120, 180 minutes) and on the y axis is the concentration of Pt in mg/L. The sonoelectrochemistry improved the dissolution rate of platinum for each experiment. In the last experiment (180 minutes), the platinum concentration in the electrolyte was almost doubled (i.e. 27 mg/L vs 16 mg/L). Fig. 8 shows the power of ultrasounds to achieve larger dissolution rates.

Sample ID	Catalyst de electro	Metal's d in 5	issolution 0mL	Efficiency (%)		
	Pt (μg) Pd (μg)		Pt (μg)	Pd (μg)	Pt (µg)	Pd (µg)
Conventional potential step	3.77	11.14	0.5	1.55	13.26	14
Sonoelectrochemistry potential step	2.39	7.08	0.85	2	35.4	28.2

Table 3. The concentration of electrochemical dissolution of palladium/platinum



Fig. 8. Amount of platinum dissolution from electrochemical methods in 10mL (PS and PS + sonoelctrochemistry

# CONCLUSIONS

- The results underlined the importance of chlorides in accelerating platinum dissolution
- Potential step chronoamperometry (PS) is the best electrochemical method for metal dissolution
- Almost 100% efficiency was achieved for Pt nanoparticles
- Sonoelectrochemistry doubled the metal dissolution rate from the spent catalytic converter.

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# PHENOL ADSORPTION ON NOVEL HYBRID SILICAS WITH COVALENTLY ATTACHED OLIGOSACCHARIDE UNITS

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#### ABSTRACT

A novel hybrid silicas with covalently attached oligosaccharide units were successfully synthesized by hydrothermal sol-gel condensation of tetraethyl orthosilicate and functional silanes in the presence of cetyltrimethylammonium bromide template. Three types of functional silanes were prepared by coupling  $\beta$ -cyclodextrin to (3-aminopropyl)triethoxysilane using N,N'-carbonyldiimidazole as linking agent. Enhanced content of covalently attached oligosaccharide groups onto silicas' surface was observed with increasing of ethoxysilyl constituent in  $\beta$ -cyclodextrin-silane used for sol-gel synthesis. This was confirmed by the results of IR spectral and chemical analysis of surface compounds. The structure of hybrid silicas was characterized by X-ray diffraction, nitrogen adsorption-desorption measurements, transmission electron microscopy, and dynamic light scattering. Adsorption experiments were carried out to study the effect of oligosaccharide groups immobilization on silica surface on phenol uptakes from water. The adsorption behavior of phenol in aqueous solution as a function of time and equilibrium concentration was realized by multibatch method with further UV-vis spectrophotometric analysis. Experimental kinetic curves of phenol adsorption on hybrid silicas were compared with theoretical models of Lagergren and Ho-McKay. Langmuir and Freundlich isotherm models were used to evaluate adsorption processes and parameters. It was shown that Freundlich model is appropriate for fitting the equilibrium sorption of phenol on synthesized hybrid silicas. It was proved that oligosaccharide units covalently attached to silica surface contribute to the removal of phenol from aqueous solutions. Obtained  $\beta$ -cyclodextrin-containing MCM-41 silicas could be very promising for phenol uptakes from aqueous solutions in water treatment processes.

Keywords: nanomaterials, MCM-41 silicas, β-cyclodextrin, adsorption, aromatics

### **INTRODUCTION**

Efficient removal of pollutants from aqueous solutions is one of the most important topics in modern environmental studies because of incessant contaminants increasing in aquatic environment and drinking water. Phenol is one of the most hazardous pollutants of water due to its relatively high solubility, poor biodegradability, and high toxicity. Phenol is a common contaminant of aquatic environment since it is widely used in chemical industry as solvent and component of precursors, explosives, dyes, pesticides and in production of polymeric resins, disinfectants and antioxidants [1]. Phenol may cause several diseases, eye and skin damage; irritate nose, throat and lungs; affect the central nervous system, liver and kidneys. Repeated or prolonged exposure to phenol can cause headache, nausea, dizziness, difficulty in swallowing, diarrhoea or vomiting [2]. Given in attention that chlorination of natural waters for disinfection produces dangerous chlorinated derivatives, phenol could be harmful to human being and animals even at low concentration. Therefore, there is a need for productive and economically advisable methods for complete removal of phenol from wastewaters and ground waters.

In general, there are two pathways for the removal of phenol from aqueous solutions – destruction of aromatic in water and its separation from water. Destruction technologies includes non-catalytic and catalytic wet air oxidation, oxidation with enzymes, ozone, hydrogen peroxide, chlorine dioxide, potassium permanganate, electrochemical and photocatalytic oxidation, supercritical wet gasification, application of electrical discharges, sonification, and

biochemical treatment [3]. Nowadays, the combination of different destruction processes is frequently used to improve phenol degradation, for example, catalytic wet peroxide oxidation with sonication, ozonation with UV irradiation, high-powered acoustic with ozone and hydrogen peroxide oxidation [4]. The common methods of phenol separation from water solutions are steam distillation [3], extraction [5-8], membrane treatment [9-12], and adsorption. The last one seems to be a good choice due to its operational ease, high efficiency, and cost-effectiveness [3]. Various adsorbents were used to treat phenol-containing aqueous solutions, such as polymers (adsorption capacity from 33 to 240 mg/g) [13-16]; modified bentonites (adsorption capacity 117 and 333 mg/g) [17, 18]; apatite [19] and hematite [20] with moderate adsorption capacity 8 and 16 mg/g, respectively; chitosan containing adsorbents (adsorption capacity 243 mg/g) [21, 22]; carbon nanotubes [23, 24], and other nanocomposites [25-28]. In recent years, low-cost natural adsorbents (rice hush, coconut coir, tea leaves, shells, red mud, coal fly ash, biomass, soils, zeolites) have gained increasing interest, since they are inexpensive locally available materials with sufficient removal capabilities for phenol [29, 30]. Nevertheless, amongst a large number of current available adsorbents, activated carbons are the most widely utilized materials on phenol uptakes from water because they possess a large surface area and high adsorption capacity (which is several times higher than the known ones) [3, 22, 31]. However, its wider application is restricted due to the nonselectivity, high costs for regeneration and relatively poor mechanical strength. In addition, most of the available adsorbents for phenol removal from aqueous solutions are ineffective at very low concentrations of aromatics in water. Thus, it is important aspect to develop economical and efficient adsorbents.

Mobile Crystalline Materials (MCM-41) are ordered silica materials synthesized via liquid crystal templating mechanism by subsequent removal of the organic template by calcination or acid dissolution [32]. High surface area and regular channel type structures, large pore volume and diameter, excellent hydrothermal, thermal and hydrolytic stabilities, active silanols on the surface of MCM-41 silicas make them an interesting alternative to the usage of activated carbons for phenol removal. Moreover, to yield ordered materials as promising candidate for the water treatment it is necessary to modify the surface of silica with highly active and/or selective groups, which increases the efficiency of adsorption. In this study, supramolecular approach of the synthesis of MCM-41 silicas with oligosaccharide units was used for obtaining nanoporous materials with high affinity to phenol in aqueous solutions. Here, the unique ability of cyclic oligosaccharide β-cyclodextrin to form inclusion complexes with different compounds, combined with hexagonally ordered mesoporous structure of silicas, offers attractive opportunities. To elucidate the contribution of oligocahharide units as supramolecular centers into the properties of synthesized nanoporous hybrid materials, the sorption of phenol from aqueous solutions on pristine MCM-41, amino- and β-cyclodextrinfunctionalized MCM-41 silicas was studied as a function of time and equilibrium concentration.

### METHODOLOGY

Hybrid silicas with covalently attached oligosaccharide units were prepared by sol-gel method following previously described procedure [33]. In particular, synthesis of hybrid silicas consists of three steps: (1) functional silane synthesis by coupling  $\beta$ -CD (99 %, Acros Organics) to (3-aminopropyl)triethoxysilane (APTES) ( $\geq$ 99%, Merck) using N,N'-carbonyldiimidazole (CDI) ( $\geq$ 99%, Merck) as linking agent, (2) co-condensation of functional silane with tetraethyl orthosilicate (TEOS) ( $\geq$ 99%, Merck) in the presence of cetyltrimethylammonium bromide (CTAB) ( $\geq$ 97%, Merck) template, and (3) extraction of template from pore channels of hybrid silicas in acid/ethanol solution (Scheme 1). Three types of hybrid silicas (Hybrid silica 1, Hybrid silica 2, and Hybrid silica 3) were obtained according to the composition of reaction

mixture used in  $\beta$ -CD-silane synthesis, where the APTES and CDI content in relation to  $\beta$ -CD increased from 1 : 1 to 3 : 1 and 5 : 1, respectively .



Scheme. 1. Synthesis of hybrid silicas with covalently attached oligosaccharide units

Chemical structure of synthesized hybrid silicas was confirmed by FT-IR spectroscopy (Thermo Nicollet NEXUS FT-IR spectrophotometer), potentiometric titration for aminopropyl fragments verification (Ionometer I-120.1), and estimation of  $\beta$ -CD-containing groups by acid hydrolysis to glucose with further colorimetric determination by UV-spectrophotometry (Specord M-40, Carl Zeiss, Jena). The structure of synthesized MCM-41 silicas was characterized by X-ray diffraction (DRON-4-02 diffractometer with CuK $\alpha$  radiation and nickel filter), low temperature adsorption-desorption of nitrogen (Kelvin-1042 Sorptometer), transmission electron microscopy (TEM) (JEM JEOL 1230 electron microscope operated at 100 eV). Dynamic light scattering (DLS) (Malvern Zetasizer, Version 7.11) was used to evaluate hydrodynamic size of silicas' particles.

Multibatch adsorption tests were carried out to examine the efficiency of synthesized adsorbents toward phenol uptakes from water at room temperature. In order to evaluate the effect of different organic functional groups on the surface of silicas, Hybrid silica 1, Hybrid silica 2, and Hybrid silica 3 as well as early-synthesized pristine MCM-41 and NH<sub>2</sub>-MCM-41 silicas [34] were applied to the adsorption of phenol from aqueous solutions as a function of time and equilibrium concentration.

In kinetic experiment, series of air-dried silica batches (0.02 g) were placed in stoppered glass vials and 10 ml of 0.64 g/L phenol was added. The suspension were stirred for predetermined time intervals, then the concentration of phenol in aliquots (took with PVDF)

membrane syringe filter (Millipore),  $d = 0.2 \mu m$ ) was determined by measuring the optical density with UV-Vis Specord M-40 spectrophotometer.

Adsorption isotherms were obtained by adding 0.02 g of air-dried silica adsorbents to airtight vials, and aqueous solutions of phenol with predetermined concentration (from 0.06 to 0.64 g/L) were added. After the adsorption equilibrium was reached, solutions were separated by syringe filters.

Phenol concentration in each solution from kinetic and equilibrium experiments was analyzed by UV-spectrophotometry at  $\lambda = 270$  nm. The contents of aromatic compound in filtrates were calculated from calibration curves.

The amount of phenol adsorbed on MCM-41 silicas from water was evaluated as:

$$a = \frac{(C_0 - C_f)V}{mS_{BET}},$$

where a – adsorption, mmol/m<sup>2</sup>;  $C_o$  – initial concentration of aromatic compound in aqueous solution, mmol/L;  $C_f$  – concentration of aromatics in filtrate, mmol/L; V – volume of the aqueous solution of phenol, L; m – mass of adsorbent, g;  $S_{BET}$  – BET specific surface area of adsorbent, m<sup>2</sup>/g.

### **RESULTS AND DISCUSSIONS**

### Structure of synthesized hybrid silicas with covalently attached oligosaccharide units

Synthesized hybrid silicas with covalently attached oligosaccharide units were structurally and chemically characterized in detail in our previous research paper [33, 34]. In brief, transmission spectra of hybrid silicas for pressed pellets in the range from 4000 to  $400 \text{ cm}^{-1}$  showed the absorption bands corresponding to the valence bond vibrations of immobilized oligosaccharide units (1450, 2938 cm<sup>-1</sup>), carbonyl group (1338, 1696 cm<sup>-1</sup>), and deformation vibration of amino groups (1540 cm<sup>-1</sup>). The presence of organic component (cyclodextrin and/or aminopropyl functional groups) was proved by quantitative chemical analysis of silica materials (Table 1). Several techniques were applied to elucidate the influence of organic modifiers on the MCM-41 silicas' porous structure, such as X-ray diffraction, TEM, and low-temperature nitrogen adsorption-desorption. It was shown that the intensity of (100) reflection on X-ray patterns decreases in order Hybrid silica 1 > Hybrid silica 2 > Hybrid silica 3 (Fig. 1). Hence, the increase in APTES as well as CDI comparatively to  $\beta$ -CD in the organosilane reaction mixture leads ultimately to the lowering or complete loss of hexagonally ordered mesoporous structure.



Fig. 1. X-ray diffraction patterns and TEM images of hybrid silicas

Structural parameters of mesoporous silicas calculated from X-ray diffraction peak and nitrogen adsorption-desorption isotherms are shown in Table 1. Also, average hydrodynamic diameters of silica particles and polydispersity indexes for hybrid silicas obtained by DLS measurements were represented.

Type of	X- diffra	ray action	Nit	rogen ao desori	lsorption- otion	Dynamic light scattering		Chemical analysis	
silica	d <sub>100</sub> , nm	a, nm	S <sub>BET</sub> , m <sup>2</sup> /g	V <sub>t</sub> , cm <sup>3</sup> /g	D <sub>DFT</sub> , nm	PDI	D <sub>parcticles</sub> , nm	[NH2], μmol/m <sup>2</sup>	[β-CD], μmol/m <sup>2</sup>
MCM-41	4.17	4.82	995	0.75	3.7; 5.1	-	-	-	-
Amino- silica	4.02	4.64	523	0.86	3.7; 5.1	-	-	0.84	-
Hybrid silica 1	4.11	4.75	812	1.06	3.9; 5.1	0.94	451	0.06	0.02
Hybrid silica 2	3.93	4.54	512	0.60	2.5; 3.3; 5.1	0.98	714	0.21	0.14
Hybrid silica 3	4.11	4.74	457	0.69	2.4; 3.1; 4.7	0.39	651	0.26	0.21

Table 1. Chemical composition and structural parameters of synthesized silicas

Obtained hybrid silicas with covalently attached oligosaccharide units have sufficiently high surface areas (457–812 m<sup>2</sup>/g), pore volumes (0.60–1.06 cm<sup>3</sup>/g) and  $\beta$ -CD group content (0.02–0.21  $\mu$ mol/m<sup>2</sup>), which may enhance their adsorption properties in comparison with pristine MCM-41 and NH<sub>2</sub>-MCM-41 silicas. Moreover, the  $\beta$ -CD content in these materials are comparable to those of typical CD-containing adsorbents for aromatic compounds removal from aqueous solutions [35-37].

### Phenol adsorption on $\beta$ -CD-MCM-41 silicas from aqueous solutions

Adsorption process is strongly affected by the chemistry and the surface morphology of adsorbent. Amongst the wide range of adsorbents for decontamination applications, silicas received particular attention of the researcher because of their porous texture, high surface area and mechanical stability as well as chemical reactivity of their hydrophilic surface due to presence of silanol groups [38]. However, unmodified silicas do not have good adsorption

affinity to phenol [39]. In order to increase adsorption properties toward phenol, the silica surface is often modified with hydrophobic functional groups [40-42].

In this research, to make the silica a promising candidate for water treatment, excellent surface characteristics of MCM-41 silicas, such as large surface area, well-defined pore size and shape, were combined with surface modification by amino and oligosaccharide groups. Amino groups present on the surface have high energy of adsorption and charge association and are very effective for the adsorption of organic compounds, while  $\beta$ -CD demonstrate quite particular properties due to the hydrophilic outer surface and hydrophobic lining of the central cavity, that enables it to form inclusion complexes of host-guest type with aromatics. Adsorption experiments were carried out to study the effect of  $\beta$ -cyclodextrin groups' attendance in silica matrix on phenol uptakes from aqueous solutions. In order to estimate equilibrium adsorption time for the uptake of phenol from aqueous solutions by investigated silica materials, time-dependent sorption studies were performed, whereas theirs adsorption ability was characterized in terms of adsorption isotherms (Fig. 2).



Fig. 2. Kinetic curves (a) and isotherms (b) of phenol adsorption on MCM-41 (1), NH<sub>2</sub>-MCM-41 (2), hybrid silica 1 (3), hybrid silica 2 (4), and hybrid silica 3 (5)

The uptake of aromatic molecules by all silicas was rapid, reaching equilibrium after 1 hour. For pristine MCM-41 silica, two different types of adsorption sites exist on the surface: low adsorption energy of less polar siloxane groups and high adsorption energy of polar silanol groups. NH<sub>2</sub>-MCM-41 silica have additional adsorption sites (amines groups) that could form a hydrogen bonding with phenol, thus resulted in higher activity of this adsorbent. Compared with silicas without oligosaccharide units, the presence of covalently attached  $\beta$ -CD on the surface of hybrid materials increases the sorption capacity of phenol, showing clearly that synthesized solids present a stronger affinity towards aromatics. This result can be directly ascribed to the formation of inclusion complexes with phenol inside an accessible cavity of  $\beta$ -CD, immobilized on the surface of mesoporous silicas. Moreover, as the quantity of immobilized oligosaccharide groups increases, the adsorption ability in a series of adsorbents Hybrid silica 1 < Hybrid silica 2 < Hybrid silica 3 rises for phenol removal from water.

The pseudo-first and pseudo-second order kinetic equations (linear forms) were used to analyze the adsorption processes on mesoporous silicas, respectively:

$$\lg(a_t - a_t) = \lg a_{eq} - \frac{k_1}{2.303}t$$

$$\frac{t}{a_t} = \frac{1}{k_2 a_{eq}^2} + \frac{1}{a_{eq}} t$$

where  $a_{eq}$  and  $a_t$  – amount of phenol adsorbed at equilibrium and at time *t*, mmol/g;  $k_I$  and  $k_2$  – rate constants of pseudo-first and pseudo-second order adsorption processes, 1/min and g/mmol  $\cdot$  min, respectively.

The calculated adsorption capacities at equilibrium, rate constants and regression coefficient values are listed in Table 2.

Lagergren model			Ho-McKay model			
Type of silica	k <sub>1</sub> , 1/min	a <sub>eq</sub> , mmol/g	R <sup>2</sup>	k₂, g/mmol ∙ min	a <sub>eq</sub> , mmol/g	R <sup>2</sup>
MCM-41	0.006	0.014	0.85	2.039	0.057	0.99
NH <sub>2</sub> -MCM-41	0.005	0.002	0.34	14.30	0.025	0.99
Hybrid silica 1	0.002	0.003	0.74	68.14	0.041	0.98
Hybrid silica 2	0.002	0.005	0.84	0.496	0.227	0.99
Hybrid silica 3	0.003	0.031	0.32	0.834	0.269	0.99

Table 2. Kinetic parameters of phenol adsorption on synthesized MCM-41 silicas

A linear forms of the Langmuir and Freundlich equations, respectively, were used to determine isotherms parameters:

$$\frac{C_{eq}}{a_{eq}} = \frac{1}{a_m K_L} + \frac{C_{eq}}{a_m} \qquad \text{ lg } a_{eq} = \lg K_F + \frac{1}{n} \lg C_{eq}$$

where  $C_{eq}$  is the equilibrium concentration of adsorptive in a solution, mmol/L;  $a_{eq}$  is the equilibrium adsorption, mmol/g;  $K_L$  is the Langmuir constant that characterizes the adsorption energy, L/mmol;  $a_m$  is the adsorption capacity of monolayer, mmol/g;  $K_F$  is the Freundlich constant, L/g, and 1/n is the Freundlich constant characteristic of adsorption intensity. Calculated parameters from both models are summarized in Table 3.

Table 3. Equilibrium mo	lel parameters fo	r phenol adsor	ption on s	ynthesized MCM-4	1 silicas
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Langmuir model				Freundlich model			
Type of silica	K <sub>L</sub> ,	a <sub>m</sub> ,	<b>R</b> <sup>2</sup>	K <sub>F</sub> ,	n	<b>D</b> <sup>2</sup>	
	L/mmol	mmol/g		L/g		N	
MCM-41	-0.071	-0.032	0.48	0.002	0.737	0.89	
NH <sub>2</sub> -MCM-41	-0.058	-0.034	0.21	0.003	1.035	0.71	
Hybrid silica 1	0.106	0.106	0.80	0.010	1.219	0.98	
Hybrid silica 2	0.093	0.280	0.84	0.026	1.332	0.99	
Hybrid silica 3	0.174	0.215	0.93	0.035	1.577	0.99	

Obtained results indicate that pseudo-second order kinetic model provided better correlation coefficients than the pseudo-first order kinetic model for the adsorption of phenol for all silicas, while Freundlich isotherm was more suitable for expressing the adsorption of phenol on synthesized hybrid silicas. This assumed that the adsorbent surface is heterogeneous with stronger and weaker binding sites.

### CONCLUSIONS

Hybrid MCM-41 silicas with immobilized  $\beta$ -CD moieties were synthesized by templateassisted hydrothermal co-condensation of organosilane and tetraethyl orthosilicate. Three types of materials were prepared with different content of attached functional groups. Adsorption experiments were carried out to study the effect of  $\beta$ -CD groups' attendance in silica matrix on phenol uptakes from aqueous solutions. Prepared hybrid silicas demonstrate high affinity (equal to natural minerals and low-cost natural adsorbents) to phenol due to oligosaccharide units localized on their surface. The proposed supramolecular approach of the synthesis of silicas with oligosaccharide units may be applicable for obtaining nanoporous materials with high affinity to aromatics in water treatment.

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# X-RAY DIFFRACTION STUDY OF LIQUID STRUSTURE OF AL-CO-SN ALLOYS

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#### ABSTRACT

The structure of ternary Al-Co-Sn liquid alloys has been investigated along Al<sub>25</sub>Co<sub>75-x</sub>Sn<sub>x</sub> and Sn-Al<sub>71</sub>Co<sub>28.5</sub> sections by means of X-ray diffraction and Reverse Monte Carlo simulation. The quantitative parameters have been calculated from experimental total and partial structure factors and g(r) functions including nearest interatomic distance  $R_1$ . We propose the priority influence of energy factor on the formation of melt structure due to the significant difference in the energies of Al-Co and Co-Sn interactions and competition between Al and Sn atoms in the formation of the local structure around Co atoms. As a result, Sn atoms are forced out to the periphery of the nearest environment of Co and form clusters with structure similar to the liquid tin. It has been found that the composition of Co was less than 10 at. % in local environment of Sn atoms. The structure of the ternary melts can be described as microheterogeneous. An atomic size effect has an impact on the local atomic structure of the liquid Al-Co-Sn alloys due to prominent difference in atomic radiuses of Al (1.58 A), Co (1.25) and Sn (1.58 A). The impact of the energy factor and the atomic size effect on the local atomic structure is manifested on the shape of main peak on the experimental total structure factor curves in the form of hump at small-Q values. This hump begins to appear on the S(Q) of liquid alloys at tin content more than 14 at. %. A further growth in Sn content results in transformation of the hump at small Q values into main peak for liquid alloys with Sn content more than 55 at. %. The position of this main peak is consistent with the position of main peak on S(Q) of liquid tin. It should be noted that the total S(Q) and partial  $S_{Sn-Sn}(Q)$  structure factors for liquid alloys ( $\chi_{Sn} > 55$  at/%) coincided with the S(Q) of liquid tin. The X-ray diffraction results are in agreement with the enthalpies of mixing for liquid ternary Al-Co-Sn alloys that have been calculated by model of a regular solution using Redlich-Kister-Mugianu formalism.

Keywords: Al-Co-Sn, melt, inhomogeneous structure, X-ray diffraction, RMC simulation

### **INTRODUCTION**

Reaction of aluminum with water is a cheap, efficient, environmentally friendly, accessible, and safe method of producing hydrogen [1-3]. Despite of high activity of aluminum the process is usually limited by the formation of the passive oxide film on the surface of pure metal and its alloys. Possible ways to remove protective layer are using melts or water vapor; ball-milling method to obtain fine powders; low-melting-point metals (Ga), active metals (Ca) or other additives. The powders with core/shell microstructure, which was caused by the stratification of multicomponent melts based on aluminum and low-melting metal, were found to demonstrate excellent activity for H<sub>2</sub> production [4-5]. Binary Al-Sn system has a miscibility gap in a wide range of concentrations [6] and can be a good candidate for developing powders with desired microstructure. The addition of a third component can be justified if specific microstructure is formed due to increase or decrease of miscibility degree or stability in the melt. Therefore, we decided to investigate the effect of Co addition on the formation of the structure of ternary Al-Sn-Co melts.

The aim of present study is to uncover the influence of interatomic interactions in boundary binary melts on the structure of Al-Co-Sn melts. The Al-Sn melts have endothermic values of enthalpy of mixing ( $\Delta H_{mix}$ ) [7] and noticeable positive deviations of nearest

interatomic distance R<sub>1</sub> from additivity [8], which indicates the priority of interaction between atoms of the same type on the structure and thermodynamic properties in binary melts. Experimental and model investigations [8] have shown the existence of microinhomogeneous (quasi-eutectic) structure in the range 5 – 35 at. % Sn adjoining the structurally homogeneous solutions based on aluminum and tin. At mole fraction  $\chi(Sn) \ge 35$  at. % the total S(Q) and partial S<sub>SnSn</sub>(Q) structure factors of binary alloys almost coincide with the corresponding curve for liquid tin, indicating the existence of a structurally homogeneous solution of aluminum in this concentration range. Mentioned results are consistent with data from a low-angle X-ray scattering study [9], where the existence of microgroupings of Sn atoms with a maximum radius of 10 Å was confirmed at 20 <  $\chi(Sn)$  <30 at. %.

The concentration dependence of R<sub>1</sub> for Co-Sn melts has alternating deviations from additivity: positive at  $\chi(Co) < 50$  at. % and negative at  $\chi(Co) > 50$  at. % [10], which indicates more intensive interactions between unlike atoms and correlates with negative values of enthalpy of mixing ( $\Delta H_{max}$ = -7.82 kJ/mol at 1173 K, 59 <  $\chi(Co)$  <61 at. %) [11]). For solid intermetallic in the order CoSn<sub>2</sub>→CoSn→Co<sub>3</sub>Sn<sub>2</sub> the average distance  $\overline{R_1}$ (Co-Sn) decreases from 2.843 Å (CoSn<sub>2</sub>) to 2.619 Å (CoSn) and 2.588 Å (Co<sub>3</sub>Sn<sub>2</sub>) due to increase of covalent component in Co-Sn interactions [12]. This explains the existence of a correlation for Co-Co and Co-Sn coordination in the local environment of melt with 40 at. % Sn and intermetallic Co<sub>3</sub>Sn<sub>2</sub> [10].

A further increase in the intensity of heteroatomic interactions takes place for Al-Co melts, which has significant negative deviations of additivity for the concentration dependence of R<sub>1</sub> [13] and increase of enthalpy of mixing ( $\Delta H_{max}$ = -32.5 kJ/mol at  $\chi$ (Co) = 44 at. %) [14]. Intermetallics in Al-Co systems were found in the aluminum-rich region [15] and the shortest distances are in Co-Al atomic pairs with mixed metal-covalent interactions. For example,  $\overline{R_1}$ (Al-Sn) is 2.466 Å for Al<sub>9</sub>Co<sub>2</sub> (monoclinic crystal system), 2.560 for Al<sub>13</sub>Co<sub>4</sub> (orthorhombic), 2.510 Å for Al<sub>5</sub>Co<sub>2</sub> (hexagonal) and, finally, 2.478 Å for AlCo (cubic) [12, 16-19]. Given values are shorter than the sum of atomic radii for Al (1.43 Å) and Co (1.25 Å) [20]. This explains the sharp decrease of  $R_1$  for Al-Co melts with an increase of Co content ( $R_1$  = 2.56 Å at  $\gamma(Co)=20$  at.%) and shortest partial distances R<sub>1</sub>(Co-Al) in the whole concentration range [13] due to preservation of the type of interatomic interactions in Al-Co pairs during melting. The significant energy difference of heteroatomic interactions in Co-Sn and Co-Al pairs yields the competition between Sn and Al atoms in the formation of the local environment around cobalt atoms, which is enhanced by the priority of interactions between atoms of the same type ( $\Delta H_{max}$ = ~4.1 kJ/mol) in Al-Sn melts [7] and noticeable difference in the atomic radii of Al (1.43 Å), Co (1.25 Å) and Sn (1.58 Å) [20]. In our opinion, energy and size factors explain the absence of ternary compound in the Al-Co-Sn phase diagram and phase equilibria are determined by the present boundary binary compounds [21].

In order to analyse the influence of mentioned factors on the formation of the structure in Al-Co-Sn melts we studied melts along Sn-Al<sub>71,5</sub>Co<sub>28,5</sub> ray and Al<sub>25</sub>Co<sub>75-x</sub>Sn<sub>x</sub> ( $0 \le x \le 75$ ) section. The structure of boundary melts Al<sub>71,5</sub>Co<sub>28,5</sub> and Al<sub>25</sub>Sn<sub>75</sub> have been investigated by us earlier [8, 13]. Instead of data for Al<sub>25</sub>Co<sub>75</sub> melt, we used structure parameters of Al<sub>30</sub>Co<sub>70</sub> melt [13] for analysis of melt structure along Al<sub>25</sub>Co<sub>75-x</sub>Sn<sub>x</sub> section.

### METHODOLOGY

The investigated samples have been prepared by melting pure components (aluminum (99.98 %), cobalt (99.98 %), tin (99.999 %)) in an induction furnace under a protective Ar atmosphere. X-ray diffraction experiments were performed with a high-temperature automatic  $\theta$ - $\theta$  diffractometer in Bragg-Brentano geometry with MoK $\alpha$ -radiation and scanning interval  $6-90^\circ$ . Samples were placed in alumina crucibles under a protective He atmosphere and heated

up to 1350°C or temperatures on 50°C above liquidus for high-melting samples. The obtained intensity curves were processed considering dispersion corrections for atomic scattering factors [22-23], the angular dependence of incoherent scattering [24] and polarization for structure factors (SF) calculation. Pair distributions functions (PDF) g(R) were calculated according to the equation:

$$g(R) = 1 + \frac{1}{2\pi^2 R \rho_0(\sum n_i K_i)^2} \int_{Q_1}^{Q_2} Q[S(Q) - 1] \sin(QR) dQ , \qquad (1)$$

where  $\rho_0$  – melt density, S(Q) – structure factor,  $Q = 4\pi \sin \theta / \lambda$ – diffraction vector ( $\theta$  – scattering half angle,  $\lambda$  – X-ray wavelength,),  $n_i$ ,  $K_i$  – atomic fraction and relative scattering coefficient of the atoms of *i* component. The structure models of the investigated melts were reconstructed using Reverse Monte Carlo (RMC) simulation [25] in order to calculate partial structure factors  $S_{ij}(Q)$ .

### **RESULTS AND DISCUSSIONS**

The experimental structure factors and pair distribution functions for melts along  $Sn-Al_{71,5}Co_{28,5}$  ray are given in Fig.1ab. The SF and PDF for melts along  $Al_{25}Co_{75-x}Sn_x$  section are given in Fig.2ab. Concentration dependences of positions of the first peaks for SF (Q<sub>1</sub>) and PDF (R<sub>1</sub>), are given in Fig.3a for Sn-Al<sub>71,5</sub>Co<sub>28,5</sub> ray and in Fig3b for Al<sub>25</sub>Co<sub>75-x</sub>Sn<sub>x</sub> section.



Fig. 1. Structure factors (a) and pair distribution functions (b) for melts along Sn-Al<sub>71.5</sub>Co<sub>28.5</sub> ray

As can be seen, the shape and position of the first peak of SF for ternary melts go through noticeable changes with an increase in tin content. The low-Q branch of the first peak has little asymmetry at  $\chi(Sn) \le 35$  at. %, which is transformed into the main peak at  $\chi(Sn) > 35$  at. % with a position close to the first SF peak for pure liquid tin. Corresponding changes are present on the PDF curves as well, but changes affect the right branch of the first peak. The concentration dependences of Q<sub>1</sub> and R<sub>1</sub> for melts along Al<sub>71.5</sub>Co<sub>28.5</sub> ray and Al<sub>25</sub>Co<sub>75-x</sub>Sn<sub>x</sub> section are similar indicating the determinative influence of tin on the formation of melt structure regardless of the composition of initial Al-Co binary melt, the structure in which is formed by high-energy Al-Co heteroatomic interactions [13].



Fig. 2. Structure factors and pair distribution functions for melts along Al<sub>25</sub>Co<sub>75-x</sub>Sn<sub>x</sub> section



Fig. 3. Concentration dependence of the  $Q_1$  and  $R_1$  for melts along Al<sub>71.5</sub>Co<sub>28.5</sub> ray (a) and Al<sub>25</sub>Co<sub>75-x</sub>Sn<sub>x</sub> section (b)

The main reason of the listed features is the energy factor, associated with the intensity of interatomic interactions in the boundary binary Al-Co, Co-Sn, Al-Sn melts. The quantitative measure of such interactions is the enthalpy of mixing. Negative values of  $\Delta H_{mix}$  indicate the priority of the heteroatomic interactions on the formation of structure and properties of Al-Co and Co-Sn melts, while positive ones point out preferable interactions between atoms of the same type in Al-Sn melts, which explains a wide miscibility gap in supercooled state [21]. At the same time, the interaction intensity in Al-Co pairs ( $\Delta H_{max}$ = -32,5 kJ/mol) is significantly higher than in Co-Sn pairs ( $\Delta H_{max}$ = -7,82 kJ/mol), which leads to the competition between Al and Sn atoms in the formation of Sn outside the nearest environment of Co. As result, microregions with structure are formed (one type of microgroupings has tin-like ordering), which is directly reflected on the shape of the first peak of structure factor for ternary melts.

The structure features of the ordering of Sn atoms are more clearly shown on the partial structure factor  $S_{Sn-Sn}(Q)$  calculated from model cells for corresponding melts (Fig.4). At  $\chi(Sn) < 12$  at. % the  $S_{Sn-Sn}(Q)$  have distinct and high peaks, i.e., Sn atoms are statistically distributed in the melt volume and structure is defined by priority of Al-Co interactions and Sn atoms are involved in the local environment of Co atoms. At higher tin concentrations, the effect of competition between Al and Sn atoms is more prominent leading to the transformation of the

shape of the first peak due to the formation of microregions with the structure of liquid tin. Herewith at  $\chi(Sn) \ge 55$  at. % the partial structure factors  $S_{Sn-Sn}(Q)$  almost coincide with experimental SF for liquid. Analysis of the  $S_{CoCo}(Q)$ ,  $S_{AlCo}(Q)$  and  $S_{CoSn}(Q)$  partial SF indicated the statistical distribution of Co atoms in the melt at high tin concentration and the nearest environment of Co was formed mainly by Sn atoms, which corresponds to structurally homogeneous solution based on the liquid tin. Regarding intermediate region of ternary melts with  $\approx 12-55$  at. % Sn, we assumed the structure is microinhomogeneous.



Fig. 4. Partial structure factors  $S_{SnSn}(Q)$  for melts along  $Al_{71.5}Co_{28.5}$  ray (a) and  $Al_{25}Co_{75-x}Sn_x$  section (b)



Fig. 5. Enthalpy of mixing (kJ/mol) isolines for Al-Co-Sn melts at 1773 K. ⊙- compositions of the investigated melts

The results of X-ray diffraction studies and RMC simulation correlate with the enthalpy of mixing for Al-Co-Sn melts, which was calculated for the whole concentration triangle in the model of regular triangle using the Redlich-Kister polynomials and Muggianu extrapolation method [26]. As one can see from Fig.5, the maximum absolute value of  $\Delta$ H is near binary Al-Co system, which confirms the influence of Al-Co interactions and energy factor in general on

the formation of the structure of ternary melts in a wide concentration range. Small exothermic values of  $\Delta H$  at high tin content imply a significant decrease of the influence of energy factor and results in the formation of structurally homogeneous solution. Therefore, the influence of the energy factor on the formation of the ternary melts structure has a direct experimental confirmation.

## CONCLUSIONS

Energy factor in the formation of the structure of ternary Al-Co-Sn melts results in the competition between Al and Sn atoms in the formation of the local environment of Co. Three concentration regions with different structures were distinguished. At low tin content, the local structure was similar to the Al-Co melts and Sn atoms were statistically distributed in the volume. At  $\chi$  (Sn)  $\geq$  55 at. % the structure of melt was close to liquid tin with Al and Co atoms even distribution. Melts with  $\approx$  12-55 at. % Sn were microinhomogeneous.

Further research will focus on the application of the Delaunay tessellations to the obtained structure models. We plan to study additionally Al-Ni-Sn and Al-Fe-Sn melts to distinguish the influence of 3d-metal on the structure of ternary melt.

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# X-RAY DIFFRACTION STUDY OF ANORTHITE-TIALITE MIXTURES IN SOLID AND LIQUID STATES

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#### ABSTRACT

The structure of two mixtures of anorthite and tialite has been investigated by means of X-ray diffraction in a wide temperature range: from room temperature to the melting point ( $\approx 1500^{\circ}$ C). Such mixtures are used as refractory materials in the lining furnaces for metals with high melting point. Compositions of the mixtures are: 1) 10 mol% tialite + 90 mol% anorthite; 2) 15 mol% tialite +85 mol% of anorthite. The given two mixtures were studied also in the molten state at 1660°C. All measurements were carried out in a high-temperature vacuum chamber in a purified helium atmosphere. It has been found that the diffraction patterns at different temperatures in the crystalline state show reflections of various modifications of tialite and anorthite. In crystalline samples at temperatures above 1000° C, weak reflections of mullite can be identified but they are hardly distinguishable from the background. A structural model of the investigated melts has been proposed on the basis of nanocrystal discrete microformations located in a disordered diffuse matrix. The environment of the disordered part of the matrix is formed by particles (atoms, atomic clusters) that do not participate in the formation of nanocrystal microgroupings. Titanium microgroupings have small size and can sink into molten matrix due to excess density, reducing the saturation of titanium dioxide surface.

**Keywords**: Anorthite, mullite, thialite, X-ray diffraction, intensity curves, structure factor, curves of radial distribution of atoms

### **INTRODUCTION**

Melts of CaO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-TiO<sub>2</sub> system are quite commonly used in industrial processes. The slags based on this system are formed during heat processing of titanomagnetites into cast iron using blast furnaces. An overview of their properties is presented in [1]. The phase compositions of high-alumina ceramic and fireproof products are located inside tetrahedron Al<sub>2</sub>O<sub>3</sub>-Al<sub>6</sub>Si<sub>2</sub>O<sub>13</sub>-Al<sub>2</sub>TiO<sub>5</sub>-CaAl<sub>2</sub>Si<sub>2</sub>O<sub>8</sub> compositions [2]. These products are formed by annealing of raw ingredients [3].

Ukraine is one of the leaders in fabrication and usage of materials based on the CaO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> system. The collaboration between the Taras Shevchenko Kiev National University, "Technohim" company (Zaporizhia, Ukraine) and the National University of Zaporozhye is focused on detailed investigation of this system [4-6] in order to obtain more information about its structure and properties. There is an opinion that anorthite (CaAl<sub>2</sub>Si<sub>2</sub>O<sub>8</sub>) and tialite (Al<sub>2</sub>TiO<sub>5</sub>) may exist in the high-alumina ceramic at a certain temperature interval [7]. The aim of this collaboration was to perform structure and properties studies that are necessary to develop new materials based on the CaO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> and CaO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> systems.

This work is devoted to study of oxide materials based on anorthite with tialite additives in solid and molten state. The high-temperature properties of such materials are utilized as fire retardant for lining metal smelting furnaces. The high-temperature durability as well as low chemical activity at high temperature of these materials is very promising for many refractory applications.

Anorthite – tialite refractory material products have high commercial demand, which is expected to increase significantly in the near future. Unfortunately, their high melting temperatures (above 1600°C) restricts the X-ray diffraction measurements in molten state due to temperature limits of high-temperature diffractometer. However, high-temperature investigation in solid and molten states is quite necessary to develop a scientific basis of fabrication of new refractory materials based on CaO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> and CaO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> system of trial and error. Knowledge about the nature of interatomic interaction in melts has significant scientific and practical interests. It should be noted that the structure of CaO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> melts has not been widely studied due to high melting temperatures. To our best knowledge, there is no structure investigation of CaO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> melts.

The main goal of this work is to study phase transformations of anorthite-tialite materials at high temperatures as well as local atomic order of corresponding melts.

# METHODOLODGY

Synthesis of tialite. Micropowder of technical electro-corundum (grain M20) containing Fe<sub>2</sub>O<sub>3</sub> – 0.4 mass %, CaO – 0.5 mass % and TiO<sub>2</sub> - 1.7 mass % was used for synthesis of tialite. This powder was additionally shredded using "Retsh PM 400" planetary ball mill. The mix of electro-corundum and TiO<sub>2</sub> were used to form samples by hydraulic press P-250 at a specific pressure of 4 N/mm<sup>2</sup> - cylinders with sizes d'37 and h'40 mm. The resulting samples were shredded, re-formed and annealed several times. It was found by means of X-ray fluorescence that the content of impurities in the obtained samples of tialite does not exceed 0.7 - 0.9 %.

**Preparing samples for XRD investigation.** Powdered samples of anorthite and tialite were carefully grinded in the agate mortar. The resulting powders were remelted in platinum-iridium crucibles at 1700 °C. Tamman furnace with heating in a stream of purified argon was used for melting and annealing of samples. More detailed description is given in [3,4]. The contents of the crucible were released from melting by diamond instrument with working diameter much smaller than the diameter of the crucible. Bordered with the walls and bottom of the crucible parts of samples were not used in experiments. The composition of the obtained samples is presented in the Table 1.

**Methodology of X-ray diffraction experiment and SEM analysis.** The phase composition of samples at room temperature was analysed by DRON-3 and Shimadzu X-ray diffractometers. Identification of crystalline phases was done using POWDERCELL MATCH, X'Pert HighScore Plus programs.

High-temperature X-ray diffraction experiment was carried out in the vacuum chamber with samples placed in molybdenum crucible. The bottom and inner walls of the crucibles were carefully polished to minimize interaction between the sample and the crucible. The crucibles were filled with dispersed powdered material to the level of the height of the crucibles. At first stage, solid samples were examined at different temperatures before melting. For experiments at temperatures above melting point the powder was added several times and content was melted until glassy material completely fills the crucible. The calculation of density of investigated melts was performed according to procedure described in [8-9]. The design of high-temperature X-ray diffractometer is shown in [8-11].

After cooling from liquid state solid samples were studied by scanning electron microscope with microanalysis JEOL JSM-6490LV. The samples for SEM analysis were polished with a diamond in order to achieve a sub-micron finish.

## **RESULTS AND DISCUSSION**

The compositions of the investigated samples and the temperatures of the X-ray diffraction study are given in Table 1.

N⁰	Anorthite CaAlSi <sub>2</sub> O <sub>8</sub> ,	Tialite Al <sub>2</sub> TiO <sub>5</sub>	The temperature of the experiment, °C
	mass %	mass %	Before melting, After melting
1	90	10	Room temperature, 600, 800, 1000,1200, 1400,1500, <b>1660</b>
2	85	15	Room temperature,600, 800, 1000,1200, 1400, 1500, <b>1660</b>

Table 1. The sample compositions and temperature of the XRD experiment

X-ray diffraction patterns of initial samples of anorthite, tialite and initial sample No2 (see Table 1) are shown on Fig. 1. There are two diffraction patterns of anorthite: powder annealed at 1000°C (red line) [4] and remelted powder with prolonged exposure to high temperature. It can be assumed that obtained diffraction patterns are almost identical.



Fig. 1. a) XRD patterns of initial samples: (1) anorthite powder annealed at 1000°C (red line) and remelted sample (blue line); (2) tialite; (3) sample No.2. b) .- comparison of the XRD-patterns of tialite sample with tabular data (cif files) from the MATCH dataset.

Anorthite has a primitive cell (space group  $P_1$ ). At the same time, tialite is described by an orthorhombic cell (space group  $C_{mCm}$ ). It should be noted that the diffraction pattern of the sample No2 contains reflections of tialite. However, the tialite have not been found by scanning electron microscopy in this sample. It can be assumed that tialite crystals are small and located far from each other in the sample No2.

Some microphotographs obtained by SEM from mixture sample (85% anorthite, 15% tialite) are shown in Table 2. In total, X-ray spectral microanalysis of the 26 samples has been performed. For the sample "a" microanalysis is obtained from area  $3^{\times}3$  mm and its composition corresponds to anorthite + 4.98 mass % TiO<sub>2</sub>. According to this data, the content of titanium dioxide is lesser than it should be (15%). A relatively large number of TiO2 likely concentrates on the borders of the coexisting regions. The composition of the sample "b" is very close to

pure anorthite. The sample "c" corresponds to the boundary layer around the crystal silica. The composition of this layer is close to anorthite with small additions of titanium dioxide. The left area that borders silica is very similar to the composition of the area of sample "a" (close in composition to anorthite with titanium dioxide additives). In general, investigated samples have large amounts of products of tialite decomposition and possibly anorthite - SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>. Individual areas with large CaO content have not been detected.

Sample code	Composition	Microphotograph
А	35.69-Al <sub>2</sub> O <sub>3</sub> 40.19- SiO <sub>2</sub> 19.15-CaO 4.98- TiO <sub>2</sub>	
В	34.30-Al <sub>2</sub> O <sub>3</sub> 41.09- SiO <sub>2</sub> 20.34-CaO 4.27-TiO <sub>2</sub>	
С	96.79- SiO <sub>2</sub> 3.21-CaO	
D	35.95-Al <sub>2</sub> O <sub>3</sub> 40.00- SiO <sub>2</sub> 19.88-CaO 4.16-TiO <sub>2</sub>	

Table 2. Sample codes and compositions from area of microphotographs highlighted in yellow. In the first case microanalysis was performed over the whole area.

As one can see from the fig. 1, both samples of anorthite are very similar. Tialite is present on the diffractograms of the mixture sample. However, the quantitative ratio of tialite and anorthite in samples (according to X-ray quantitative analysis) is significantly less than the estimated 10 and 15 mass %. The Fig. 1 (b) shows the XRD patterns of tialite samples in comparison with calculated XRD patterns of various tialite modifications (cif files). All tialite modifications are orthorhombic with different lattice parameters. Obtained results points out that XRD patterns of tialite samples can be fully described using only several modifications of tialite.

High-temperature X-ray diffraction study of solid samples (Table 1) points out that they are mixtures of anorthite and tialite. It can be said that the ratio of the main maxima of the crystalline phases is approximately one and a half times less than 10 and 15 wt% tialite as calculated. There are some peculiarities in obtained XRD patterns that are connected with background. For example, fig.2 shows a high background. If tialites content differs only by 5 wt% in the samples, the form of the background differs substantially for all temperatures. In

addition, the background line for 10 mass % is significantly lower in intensity than the background line for 15 mass %.



Fig. 2. Isolated background for 10 mass % tialite compositions (a) and 15 mass % tialite (b).

Fig. 3 shows the temperature dependence of X-ray scattering curves for two samples with 10 (a) and 15% mas. tialite (b). The compositions of the samples are very similar, but there is difference in the background. The structure of sample with 10 mass %  $Al_2Ti_2O_5$  practically does not change with increasing the temperature up to 1200°C. Some structure transformation takes place at 1400°C. The decomposition (possibly partial) of complex substances into simple oxides begins at 1500 °C.

Some peaks of the XRD pattern at 1500 °C belongs to  $SiO_2$ ,  $Al_2O_3$ ,  $TiO_2$  and mullite. There are peaks that can be identified as CaO phase but with low probability. It was found that the location and intensity of peaks at high temperatures changes over time thus complicating phase analysis.

X-ray scattering curves obtained at room temperature and 600, 800, 1000 °C for sample with the composition of 15 mass % tialite (Fig. 3.b) differ from each other. These differences point out that some structural ordering occurs during increasing temperature up to  $600^{\circ}$ C.



Fig. 3. X-ray scattering curves of samples with 10 mass % tialite (a) and 15 mass % tialite (b). 1 - room temperature, 2 - 600, 3 - 800, 4 - 1000, 5 - 1200, 6 - 1400, 7 - 1500°C. Anorthite peaks are indicated by (\*) and tialite by (\*). Monoclinic anorthite formed at 800 and 1000 ° C for the composition 15 mass% Al2Ti2O5 is indicated by (+).

Further increasing in temperature leads to changes in the structure. At 1500°C these changes are associated with the partial disintegration of the main phases of tialite and anorthite to simple oxides. Some peaks can be interpreted as mullite. More accurate conclusion about phase transformations cannot be made due to the instability of the structure over time. It should be noted that at high temperatures some reflections have a high intensity at large angles of scattering. Perhaps the increase in temperature leads to the formation of nanoclusters, which are oriented by certain planes parallel to the surface. This phenomenon can lead to an increased height of diffraction peaks at large scattering angles

It was found that XRD curves of two investigated samples at  $1500^{\circ}$ C are very different (Fig 3 a,b). The composition with 10 % of tialite is obviously more resistant to high temperature. Its structure practically does not change with increasing temperature up to  $1200^{\circ}$ C. Partial decomposition occurs at  $1400^{\circ}$ C. However, the XRD pattern changes significantly at  $1500^{\circ}$ C. The analysis shows that a complete disintegration of complex compounds with the formation of simpler ones takes place at  $1500^{\circ}$ C.



Fig. 4. X-ray scattering intensity curves (IC) of molten samples with 10 mass % tialite (a) and 15 mass % tialite (b) at 1660°C. All curves are obtained at the same temperature, 1,2,3 - the number of the run.

Fig. 4 shows intensity curves of two investigated samples at 1660°C (after melting). The number near each curve is the number of the run. Usually, these six curves should be similar and their shape should resemble curves 2 without any crystalline peaks. The X-ray scattering intensity curve during first run have similar crystalline peaks. Presence of these peaks can be explained by residual crystalline phenomena near melting temperature. They disappear after long isothermal exposure at 1660°C. As a result the ICs (second run) have typical form for melts. The appearance of crystal peaks in both ICs (third run) was unexpected. This phenomenon will be investigated in the near future.



Fig. 5. The structure factor (a) and the radial distribution function (b) of melt with 10 mass % tialite (1 and 2 runs).

The ICs (first and second run) have been used for calculation of structure factors (SF) and radial distribution function of atoms (RDF) (Fig.5b). The details of high-temperature study and calculation of SF and RDF is described in [8-10]. In case of IC 1 crystalline peaks have been removed before calculations of the SF and the RDF. The shape of the SF and the RDF depends on isothermal exposure at 1660°C. The analysis of the RDF was complicated by arising and disappearing of crystalline phases over time. Therefore, the conclusion about the structure of the melt has a preliminary character.

The obtained SF curves have significant differences that indicate possible structural adjustments during isothermal exposure at 1660°C. The first structural maximum of the RDF is due to the contribution of distances Si-O (0.165 nm) and Al-O (0.172 nm). These distances form the shape of the first maximum. The difference in the form of the first maximum in the second curve can be explained by the increase of the Al-O coordination from four to six. In the first case aluminum was tetrahedrally surrounded by oxygen, and in the second - octahedrally. The area and the height of the first maximum (at 0.185 nm) increases. It is known that this region is contributing to aluminum octahedrally surrounded by oxygen. Ca-O's contribution is small due to its small amount. The third maximum may be the distance of O-O. However, the coordinate coordinated oxygen number is too high. This is probably due to errors in the formation or destruction of crystalline phases.

The investigated materials are used for fabrication of as refractories. Refractories must have increased structural stability at high temperatures. Crystal-type refractories are generally stable. Small size (nano size) of crystals contributes to their interaction with aggressive environment due to a large surface layer. When interacting with other particles, nanoparticles can change their structure to grow or break down. The constant interaction of nanoparticles with other phases can lead to the instability at increased temperature.

At the same time, similar processes can occur in investigated melts. Nanoparticles can exist in the melts and they are very difficult to identify by X-ray diffraction study due to their small size. A change of the melts composition or the size of the nanoparticles during isothermal exposure can lead to growth of this nanoparticles and further crystallization process. Perhaps this phenomenon resembles vibrational reactions of the Zhabotitnsky - Belousov type [11]. It may be noted that liquid state of anorthite [7] was stable during isothermal exposure.

### CONCLUSIONS

The structure of two mixtures of anorthite and tialite ( $10 \mod \%$  tialite +  $90 \mod \%$  anorthite and 15 mol% tialite +  $85 \mod \%$  of anorthite) has been investigated by means of X-ray diffraction

in a wide temperature range up to 1500°C. The investigation of these samples in molten state at 1660°C has been performed.

It has been found that the diffraction patterns at different temperatures in the crystalline state show reflections of various modifications of tialite and anorthite. In crystalline samples at temperatures above  $1000^{\circ}$  C, weak reflections of mullite can be identified but they are hardly distinguishable from the background. It points out that structural changes are occurring in the investigated samples at  $1000^{\circ}$ C.

It was established that basic materials (anorthite and tialite) decompose (at least partially) with the formation of simple oxide phases with an increase in temperature up 1500 °C. There is also an evidence of formation of the mullite at 1500 °C.

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# CONFERENCE PAPERS

11

## II.4. Laser Technologies

Ž. Prielaidas, E. Stankevičius. INVESTIGATION OF THE OPTICAL DAMAGE
THRESHOLD OF MICROAXICONS FORMED BY INTERFERENCE LITHOGRAPHY
E. C. Erdman et al. <u>FEMTOSECOND SYNCHRONIZATION OF TWO INDEPENDENT</u> LASER SYSTEMS
M. Gaidys et al. HIGH-THROUGHPUT LASER ABLATION AND POLISHING OF
COPPER CYLINDERS

## INVESTIGATION OF THE OPTICAL DAMAGE THRESHOLD OF MICROAXICONS FORMED BY INTERFERENCE LITHOGRAPHY

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#### ABSTRACT

Here, periodic microstructures with varying geometries were made in a hybrid inorganic-organic photopolymer ORMOSIL (SZ2080) using four-beam laser interference lithography. These fabricated microstructures act like microaxicons and can be used to generate Bessel-like beams. The ideal Bessel beam cannot be experimentally realized of course, but its perfect approximation (the mentioned Bessel-like beam) can be generated over a limited distance. The characteristics of generated Bessel-like beams depend on the geometrical parameters of the fabricated structures, which can easily be controlled via the laser processing parameters. The demonstrated method enables an easy fabrication of optical tweezers, optical imaging systems, or material processing tools, which have a broad range of applications. Regarding the practical use of such microaxicons, their optical damage threshold becomes very important as well, therefore experiments for laser-induced damage threshold and laser ablation threshold of the periodic structures formed by interference lithography were performed. In parallel, the same damage threshold experiments were performed on an unstructured photopolymer coating. In this work, the experimental results related to the damage threshold assessment of microaxicons formed via interference lithography will be presented and analysed.

Keywords: interference lithography, SZ2080, ORMOSIL, Bessel-like beams, laser-induced damage threshold, laser ablation

## **INTRODUCTION**

Various periodic microstructures can be formed using interference lithography, which can even be used for the generation of Bessel beams. Of course, the ideal Bessel beam cannot be realized experimentally, but over a limited distance, its perfect approximation can be generated. This approximation is known as Bessel-like beam [1]. Due to their unique properties (non-diffractive propagation and the ability to self-reconstruct after an obstacle), Bessel beams are widely used in various practical applications: microfabrication [2], optical lithography [3], optical tweezers [4], imaging [5], etc. Typically, Bessel beams are formed by conical lenses – axicons, but nowadays it is very important to form effective microaxicons which have diameters smaller than a millimeter, because such micro-optical elements can be integrated into optical fibers [6] and used to direct Bessel beams to hard-to-reach places, for example, endoscopic tissue examination [7]. Interference lithography is a very attractive way of forming microaxicons, as this method allows the simple formation of micrometer order structures. Regarding the practical use of such microaxicons, their optical damage threshold becomes important, therefore, in this work, the studies of laser-induced damage threshold and laser ablation threshold of periodic microstructures produced by interference lithography were also performed.

## MATERIALS AND METHODS

#### Fabrication of microaxicon-like structures

Microaxicon-like elements were fabricated from a hybrid organic-inorganic negative photoresist doped with Zr called SZ2080 [8] (FORTH, Greece) and enriched with 4,4-bis(dimethylamino)-benzophenone (BIS) (concentration by a weight equal to 0.5%) using four-beam interference lithography method. The principle of this fabrication process is shown in Fig. 1.



Fig. 1. Fabrication of periodic polymeric microstructures via the four-beam interference lithography: a) irradiation of a photopolymer by the four-beam interference intensity distribution which causes polymerization in its volume; b) polymeric structure is formed which reproduces the interference intensity distribution; c) development process; d) fabricated periodically arranged microstructures

Before the fabrication process, photopolymer samples were prepared by spin-coating the photopolymer on glass substrates and heating them for ~20 min at 95 °C afterwards to evaporate the solvent and solidify the samples. For the microstructure fabrication process, a picosecond laser (CYRA Duo, AmpLight) emitting pulses with a duration of ~7 ps at 1 kHz repetition rate and 515 nm wavelength was used. Four identical laser beams were obtained using a diffractive optical element (DOE) (Holo-Or Ltd.) by splitting the laser beam. Then, these four beams were collected by a two-lens imaging system in order to generate a four-beam interference pattern (Fig. 1(a)), which initiated the photopolymerization process in the sample (Fig. 1(b)). After this step, samples were immersed into 4-methyl-2-pentanone for 10 min (Fig. 1(c)) to dissolve unmodified polymer parts and develop the periodically arranged polymeric microstuctures (Fig. 1(d)).

#### **Optical performance test**

Optical properties of the fabricated microstructures were investigated using the optical performance test system (Fig. 2). This system consists of a continuous wave HeNe laser (Meredith Instruments), telescope, sample positioning system, objective, and a CCD camera connected to a computer. The wavelength of the HeNe laser was 633 nm and the average power

was 2 mW. The magnification of the system was 19. In order to characterize the generated beams formed by the fabricated microstructures, the sample was placed before the objective at a distance larger than the focal length of the objective (11 mm), and by moving the sample in the *z*-direction the propagation of the beam behind the sample was registered.



Fig. 2. The scheme of the optical performance test system

## Laser-induced damage threshold and laser ablation threshold tests

A picosecond laser (Atlantic HE, Ekspla) emitting pulses with a duration of ~10 ps at a 400 kHz repetition rate and 1064 nm wavelength was used for the laser-induced damage and laser ablation threshold measurements. The laser beam was focused down to ~24 µm diameter at  $1/e^2$  intensity level. 1-on-1 and S-on-1 (S = 1000) regimes were used for laser-induced damage threshold measurements according to ISO 21254-2:2011 [9] standard. These tests are done by irradiating a set number of spots with a single pulse (or S number of pulses depending on the test used) with different laser fluences and then calculating the damage probability. Afterward, by plotting the damage probability as a function of laser fluence and extrapolating it until the damage probability is equal to 0, the laser-induced damage threshold value is estimated [10]. Whereas, the laser ablation threshold value  $F_{th}$  is experimentally determined from the relationship between laser fluence at the center of the beam  $F_0$  and diameter D of the crater formed by laser irradiation. By plotting  $D^2$  as a function of  $\ln(F_0)$  and extrapolating it to  $D^2 = 0$ , the laser ablation threshold value is estimated [11].

## **RESULTS AND DISCUSSION**

Using the four-beam interference lithography technique, two kinds of periodic polymeric microstructures with varying geometries were fabricated, which will be referred to as type I and II (shown in Fig. 3.).



Fig. 3. Three-dimensional photographs of formed periodic microstructure arrays taken with an optical profilometer. The black bars in the photos indicate the period of the microstructures and are equal to  $60 \,\mu m$ 

The laser parameters used for the fabrication process of both types of microstructures were the same (1.8 W average power, 20 min exposure duration) and the only difference was the revolutions per minute (rpm) used in the spin-coater (6000 and 1000 rpm for type I and type II respectively). The average height and diameter of the formed microstructures including their standard deviations were measured using the optical profilometer (Fig. 3.). The diameters of type I and II microstructures coincide within the estimated error limits, and the height difference is ~3  $\mu$ m. Judging from the fact that the peaks of both types of microstructures appear flat, it lets us understand that the maximum possible height was reached in both cases, i. e. the heights reached the value of the polymer coating thickness.

Optical performance tests were performed as described in Section 2.2. and images of the beam propagation behind both types of microstructures at different distances from the samples are shown in Fig. 4. The beams formed by type I and type II microstructures are very different because their geometrical parameters are different. It can be seen that at some distances from the sample, the intensity distributions of generated beams are similar to the Bessel beam: the beams consist of narrow and intense central maxima surrounded by equidistant rings. This shape is also a known characteristic of Bessel beam [12]. The optical performance test results show that both types of manufactured microstructures generate beams with concentric rings. This intensity distribution with a series of concentric rings alludes to the Bessel beam intensity distribution that is proportional to the square of the zero-order Bessel function of the first kind [1]:

$$I(r,\beta) \propto J_0^2(k_\perp r),\tag{1}$$

where *r* is the radial coordinate;  $k_{\perp}$  is the perpendidular wave vector component which is related to the wavelength  $\lambda$  and the half apex angle  $\beta$  of the cone by

$$k_{\perp} = 2\pi \sin\beta/\lambda. \tag{2}$$

Comparison of the average transverse intensity profiles of the beams (black lines in Figs. 5(a) and 5(b)), generated by different type of microstructures (Fig. 5(a) – type I, Fig. 5(b) – type II) at the distance of 100  $\mu$ m (Fig. 5(a)) and 260  $\mu$ m (Fig. 5(b)) from the sample with the theoretical Bessel beam transverse intensity distribution calculated using Eq. (1) when the perpendicular wave vector ( $k_{\perp}$ ) is 0.9 (red line in Fig. 5(a)) and 0.6 (red line in Fig. 5(b)) indicates that the generated beams truly have Bessel beam characteristics.



Fig. 4. Beams intensity distributions exiting from a different type of microstructures (type I (a, b, c, d), type II (e, f, g, h)) in the transverse plane at different distances from the apex of the microstructures: 40  $\mu$ m (a, e); 100  $\mu$ m (b, f); 200  $\mu$ m (c, g); 400  $\mu$ m (d, h). The scale bars represent 30  $\mu$ m



Fig. 5. Comparison of the intensity distributions of the Bessel-like beams generated using different types of microstructures: a) type I; b) type II at the distance of 100  $\mu$ m (a) and 260  $\mu$ m (b) from the sample (black lines) with the numerical fit of the Bessel beam intensity distribution when  $k_{\perp} = 0.9$  (a) and 0.6 (b) (red lines)

Lastly, laser-induced damage and laser ablation thresholds were estimated using the tests described in Section 2.3. Only type I of the microstructures was used for these tests because it generated qualitatively better Bessel-like beams. In parallel, the same damage threshold experiments were performed on an unstructured photopolymer coating, which will be referred to as type III sample, that was spin-coated using the same rpm (6000) as type I microstructures (which means that the thickness of type III sample polymer coating was roughly the same as the height of type I microstructures, i. e. ~7.4  $\mu$ m) and photopolymerized by irradiating with a UV lamp for 30 min (average power of the lamp was 11 W). Laser-induced damage threshold

measurement results and the estimated laser-induced damage threshold values are shown in Fig. 6. Laser ablation threshold measurement results and the estimated laser ablation threshold values are shown in Fig. 7. The deviations from the theoretical linear fit arise from the fact that these tests are statistical and heavily depend on the set number of irradiated spots and various surface defects, dust, cracks, etc. can lower the damage threshold. In order to get more accurate results from these measurements, the set number of irradiated spots has to be increased (in this work, this number was set to 10).



Fig. 6. Laser-induced damage threshold test results and the estimated laser fluence threshold values: a) type I, 1-on-1 test; b) type I, S-on-1 (S = 1000) test; c) type III, 1-on-1 test; d) type III, S-on-1 (S = 1000) test

Finally, the estimated laser fluence threshold values for laser-induced damage and laser ablation for type I and type III samples are summarized in Fig. 8. It was estimated that the laser fluence values for both investigated damage thresholds are lower for polymeric microstructures (type I sample) than for the polymerized unstructured polymer coating (type III sample). The damage thresholds are possibly reduced due to the shape of the fabricated microstructures, which helps to focus the laser irradiation and achieve even higher fluence values. Also, it can be seen that the error values obtained for type I samples are bigger, so in order to obtain more accurate threshold values, the scope of the tests should be increased, i. e. the set number of spots that are irradiated during the tests should be increased.



Fig. 7. Laser ablation threshold test results and the estimated laser fluence threshold values: a) type I; b) type III.  $D^2$  is the square of the diameter of the crater formed by laser irradiation



Fig. 8. Laser-induced damage threshold ("1-on-1" and "S-on-1") and laser ablation threshold ("Abl.") values of type I sample (microstructures) and type III sample (unstructured polymer coating)

### CONCLUSIONS

Periodic polymeric microstructures, fabricated using four-beam interference lithography, can generate Bessel-like beams when illuminated by laser light. The intensity distributions of the generated beams depend on the geometrical properties of the manufactured microstructures, which can easily be controlled by changing the irradiation dose: exposition duration and average power. It was found that when the diameters of the microstructures coincide within the error limits, Bessel beams generated by smaller height microstructures (~7.4  $\mu$ m) appear qualitatively better and have a longer formation area compared to bigger height microstructures (~10.2  $\mu$ m). It has also been observed that lower laser-induced damage and laser ablation threshold laser fluence values are obtained for polymeric microstructures compared to an unstructured photopolymer layer.

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## FEMTOSECOND SYNCHRONIZATION OF TWO INDEPENDENT LASER SYSTEMS

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#### ABSTRACT

One of the goals of the Extreme Light Infrastructure (ELI) project is to research and develop highbrightness, ultra-fast coherent sources. A direct application for these state-of-the-art coherent sources is pump-probe experiments, which are the cornerstone of studies in ultra-fast dynamics. The ALLEGRA laser (1 kHz, 50 mJ pulse energy, 15 fs pulse duration) developed at ELI-Beamlines in the Czech Republic is already being used for various scientific experiments. The femtosecond synchronization project (referred to as FSYNC) will dramatically improve the ALLEGRA laser pump-probe capability by developing a fully synchronized, independent auxiliary laser system inspired by the design of the ALLEGRA front end, with energy exceeding 10 mJ at 1kHz [1]. This will open the door for a number of physical processes that can be explored by allowing any arbitrary delay between pump (laser or laserdriven X-ray) and probe pulses. FSYNC also plans to explore coherent beam combination of the two synchronized laser chains in an interferometer configuration. The goals of the FSYNC project cannot be realized without a high quality electronic lock to stabilize the frequency of the master oscillators, as well as several unique balanced optical cross-correlators (different acquisition frequencies and different colours). In this paper, the FSYNC project will be introduced and the architecture of the amplifier chain will be presented. Likewise, the design of the locking systems still in the research and development process will be discussed, along with some preliminary proof of principle experiments. Finally, plans for future measurements using the flexible pump-probe laser system will be mentioned.

Keywords: femtosecond synchronization, electronic lock, balanced optical cross-correlator, coherent combination, pump-probe

## MOTIVATION OF THE FEMTOSECOND SYNCRHONIZATION PROJECT

The Femtosecond Synchronization project (known as FSYNC) will provide an auxiliary beam to the existing ALLEGRA laser system (formerly known as L1) at ELI-Beamlines. The FSYNC amplifier chain has the same laser architecture as the ALLEGRA front end [1]. This auxiliary laser system will have two functions: 1) to serve as a high energy probe pulse (10 mJ) for the main ALLEGRA output with arbitrary relative delay and 2) as a second high energy channel to investigate methods of high energy, ultra-fast coherent combination. Both FSYNC functions use the same auxiliary laser system which can be run in two configurations shown in Fig. 1. Two operational modes are possible corresponding to the two research activities, coherent combination (CC) and pump-probe (PP).



Fig. 1. Concept of FSYNC integration with ALLEGRA laser. PP mode- pump-probe mode; CC mode- coherent combination mode; BOC- balanced optical cross-correlator; CWcontinuous wavelength; AOPDF- acousto-optic dispersive filter; SC- supercontinuum; SHGsecond harmonic generation; OPA- optical parametric amplification

The next generation of light sources like ELI-Beamlines [2], European X-ray free electron laser facility (XFEL) [3], the Linear Coherent Light Source at SLAC (LCLS) [4], and the ELLETRA-Facility in Trieste [5] require femtosecond synchronization between the RF systems, the injector laser, and in some cases, the probe laser for pump-probe experiments [6]. Pump-probe experiments are the cornerstone of studies in ultra-fast dynamics and will be a critical component of research at the ELI-Beamlines facility in the future. In the current scheme, the dynamics that can be probed by this method via ALLEGRA laser-driven experiments are limited to a time-scale of nanoseconds. This is due to the fact that the probe pulse must be physically split from the pump pulse and delayed using an optical delay line. As a direct result of the FSYNC project, the number of physical processes which can be explored via pump-probe by allowing any arbitrary delay between pump (laser or laser-driven X-ray) and probe pulses will be expanded. Optical timing system based on stabilized fiber links at LCLS demonstrated overall synchronization of the x-ray and pump laser of <50 fs [7]. The FSYNC probe delay would be completely electronically controlled, eliminating the need for delay lines in the experimental hall and giving the user the maximum flexibility. In order to achieve the required synchronization between pump (ALLEGRA) and probe (FSYNC) pulses, RF synchronization will be an important technique utilized in the form of an optical master oscillator (OMO) modelocked laser tightly synchronized to the reference microwave oscillator (RMO), similar to the design of the fourth-generation light sources like XFEL [6]. However, to achieve femtosecond level synchronization, balanced optical cross-correlation (BOC) must be used in conjunction with RF synchronization. Attosecond timing jitter has been achieved using BOC to synchronize pulse trains from independent mode-locked lasers over the entire Nyquist bandwidth [8].

One of the main motivations for the research topic of coherent combination under the FSYNC project is that solid state laser gain media is reaching their technical limit; power scaling of a laser system faces obstacles associated with the degradation of efficiency and beam quality at high output powers due to thermal effects in a laser medium [9]. Coherent beam combining can be used to increase the peak intensity of high energy photon sources where technical limitations are an issue. Many different methods of coherent beam combining have been demonstrated. In fiber laser systems, light coupled into a 4x4 multicore fiber, which are then amplified and combined using segmented mirror splitters, achieved up to 70 W of combined power with a combination efficiency of 80% [10]. It has also been shown that high

combination efficiency can be achieved (89%) by coherently combining fiber amplifiers using chirped pulse amplification techniques (CPA) in two separate amplifier chains [11]. Finally, it has been demonstrated that coherent combination techniques can extend into free-space propagation. Two coherently combined OPCPA channels (optical parametric chirped pulse amplification) were overlapped in focus [12].

## **GENERAL DESCRIPTION OF THE EXPERIMENTAL SET-UP**

In order to show that we are capable of achieving femtosecond synchronization or coherent combination with the ALLEGRA laser, the construction of the FSYNC amplifier chain must be completed. This task is quite extensive. One of the major projects completed was the development of the pump laser for the OPCPA amplifier, which includes a frequency stabilized fiber oscillator (Origami), a seed distribution system completely in fiber [13], a Yb:YAG (Ytterbium doped Yttrium Aluminum Garnet) thin-disk regenerative amplifier [14], and a grating compressor. The FSYNC pump laser Emilka Double Pulse (Emilka DP) is a diodepumped thin disk regenerative amplifier using CPA and divided pulse amplification technique to obtain a 1 kHz train of high energy picosecond pulses. The 1030 nm seed pulses from the master oscillator are coupled into a polarization maintaining fiber and stretched in a CFBG (chirped fiber bragg grating) stretcher. The stretching factor of the CFBG (-350 ps/nm), as well as higher orders of dispersion, are matched to the grating compressor following the regenerative amplifier. The CFBG has a reflective bandwidth of 3.3 nm, providing a seed to the regenerative amplifier with a ~1.2 ns pulse duration. The unique characteristic of this system is that the optical seed to Emilka is in a double pulse configuration. Every millisecond, the cavity amplifies two pulses separated from each other in time by 12.5 ns. This allows for a distribution of the total energy to be between two pulses instead of one, which is helpful to avoid nonlinear effects like self-focusing.

Amplification takes place in thin Yb:YAG disks at 1030 nm. The total power extracted during the round trips is 120 mJ. The two amplified are coupled out of the cavity by a Pockels cell (PC) and subsequently separated by a second PC. The energy divided between pulse one and pulse two has a ratio of 1:3 after amplification. Even though there are two separated pulses, only one compressor is necessary. The first grating is simply wider than it needs to be for one beam only. The pulses are compressed in a Treacy compressor consisting of two MLD (multi-layer dielectric) gratings. So far, we have managed to produce amplified and compressed pulses (120 mJ with 3 ps pulse duration). In the near future, the pulses will be frequency doubled to 515 nm in lithium triborate crystals (LBO) to be the pump for 3 stages of OPCPA. Each stage includes one pass through a barium borate crystal (BBO). Stages 1 and 2 of the OPCPA will be pumped by the first frequency doubled Emilka pulse. Similarly, the second frequency doubled Emilka pulse will pump stage 3. The target pulse energy at the final stage is 10 mJ at 1 kHz compressible to <25 fs.

In PP mode, it is essential that the FSYNC OPCPA seed is derived from an independent mode-locked oscillator which is locked the microwave reference. Both the ALLEGRA oscillator and the FSYNC oscillator are locked to two channels of the master RF (radio frequency) clock, which is synchronized to an atomic clock. By electronically adjusting the phase of one of the channels relative to the other, a relative arbitrary delay can be introduced.

In order to ensure stable amplification in the FSYNC picosecond OPCPA amplifier with minimal temporal drift, the seed pulse and pump pulse should be derived from the same oscillator; this ensures perfect initial synchronization of the pump and seed pulses. We elect to use a fiber oscillator (Origami, center wavelength of 1030 nm) to seed a regenerative amplifier (Emilka DP), which will generate ps pulses to pump OPCPA. The signal for the OPCPA stages will be a broadband supercontinuum (SC) seed [15]. The process will simply be to pick-off a

small fraction of the second amplified pulse in the Emilka regenerative amplifier (several hundreds of  $\mu$ J's). This beam will then be adjusted in size and focused with a loose focus into a 13 cm long undoped YAG crystal. By changing a focal spot size with an iris and by change of energy, a stable SC can be generated, whose NIR part is used as the FSYNC seed. Its dispersion is tailored by an acousto-optic programmable dispersive filter (AOPDF or Dazzler). In such a configuration the seed beam for the OPCPA is highly synchronized with the Emilka pump pulse. The ALLEGRA front end output and auxiliary output are polarization multiplexed and spatially overlapped. Both pulses then propagate through the remainder of the ALLEGRA amplifier chain and down to the experiment. The auxiliary beam should not affect amplification in the subsequent OPCPA stages as its polarization state is not phase matched with the pump.

The coherent combination mode of operation uses a single oscillator to seed both ALLEGRA and the auxiliary beam. Because coherent combination relies on overlapping the electric field of two pulses, in practice it is necessary to start with the same laser pulse, split, amplify in two branches, and recombine. The Ti:Sapphire (Rainbow) oscillator has two outputs which are originating from the same pulse. The branch going to FSYNC will be stretched and manipulated by its own AOPDF to ensure that the total dispersion accumulated in both the ALLEGRA and FSYNC branches can be compensated accordingly. The beams are combined on a polarizer and a half-wave plate rotates the polarization by 45 degrees. The relative delay of the pulses is encoded in the polarization state of the wave and is detected by laser diagnostics at the output. The delay is optimized with a delay line and locked via the Hansch-Couillaud method [16]. The pump laser again must be synchronized to the seed in the OPCPA amplifier, so the thin disk pump laser must be seeded by the Rainbow laser in CC mode.

## DESCRIPTION OF LOCKING TECHNIQUES IN THE RADIO AND OPTICAL FREQUENCY REGIMES

## Radio Frequency (RF) Locking Technique

One of the most important requirements for high-precision syncrhonization is a master oscillator with low timing jitter [17]. After the low noise oscillator is procured, the frequency stabilization of the oscillator (for FSYNC and ALLEGRA) is an essential first step to temporally synchronize the subsequent processes that take place at a later time in the laser amplifier chain. By tightly locking the mode-locked laser to a microwave (or optical) reference, the laser serves as an OMO and the optical train is then distributed to critical optical (or microwave) subsytems [17]. For example, picosecond OPCPA requires overlap of pump and seed pulses with femtosecond precision. The coarse/slow feedback loop ensures that the phase of the seed pulses do not drift, so the arrival time of pump and seed to the nonlinear crystals can be compensated with one optical delay stage. Of course, pump-probe experiments with arbitrary delay require phase correlation between pump and probe pulses, so it's crucial that in order to meet one of the goals of FSYNC, we must have frequency stabilized oscillators (as opposed to free running).

The first task completed on the FSYNC project was to develop the new phase locking system for the ALLEGRA and FSYNC master oscillators. The first locking loop in the FSYNC experimental set-up is the coarse/slow electronic feedback loop, also referred to as NEJLock. The design of NEJLock was influenced by a successful demonstration of high-performance RF-only locking in [18]. Essentially, the Rainbow and commercial fiber oscillator (Origami) are now stabilized to the same low noise RF clock in a compact (within one rack-mountable box) configuration. The details of how the new in-house built phase locking box are as follows: an output from an RF synthesizer (frequency of 960 MHz, power amplitude of +15 dbm) was used as the reference and was connected to the input of a frequency mixer. Both oscillators operated at ~80 MHz repetition rate and the locking scheme was the same. A portion of pulse train from

the oscillator was coupled into a photodiode through an optical fiber. The photodiode has a very high bandwidth (GHz) and is optimized for the wavelength of light incident on the detector material. Therefore, the incident photons can produce several microwave harmonic combs of the fundamental frequency, which were filtered except for 960 MHz. Locking to a high harmonic decreases the noise of the locking loop, but choosing a frequency that is too high can create a lot of difficulties in the procurement of the necessary electronics with large bandwidth. The 960 MHz signal was amplified to give a strong signal, but attenuated accordingly so as to not oversaturate the RF components or the monitor oscilloscope. The 960 MHz signal from the photodiode was then used as the second input to the frequency mixer. The output of the frequency mixer went through a bias T so that the AC portion of the signal was filtered out of the mixed RF signal. The resulting DC signal is proportional to the delay offset between the oscillator cavity and the RF reference.

## **Optical Frequency Locking Techniques**

#### **Balanced Optical Cross-Correlation for Master Oscillator Synchronization**

The primary function of FSYNC is to provide a high energy probe pulse for the ALLEGRA output with arbitrary delay with femtosecond precision. This can be accomplished by stabilizing the master oscillators of FSYNC and ALLEGRA using two locking loops- the coarse/slow locking loop (NEJLock, discussed in part 3.1) and a fine/fast optical locking loop. Although it is possible to achieve femtosecond synchronization using microwave phase detection (like the method described in part 3.1), conventional synchronization based on photodiodes and mixers suffer from limited sensitivity and drifts [16]. In order to stabilize the ALLEGRA optical path length relative to the Rainbow master oscillator with femtosecond stability, BOC must be the method used to achieve this type of precision. The BOC method enables the most accurate synchronization of multiple laser sources [6, 8]. Fig. 2 below displays the optical (with the electronics) set-up of the BOC system used to show the proof of principle for femtosecond synchronization. We use a similar BOC to detect relative delays between



Fig. 2. Optical set-up of the BOC system. CMC- chirped mirror compressor; SPIDERspectral phase interferometry for direct electric field reconstruction; BBO- barium borate; SHG- second harmonic generation; SP- short-pass; FWHM- full width at half maximum; LPlow-pass; PBS- polarizing beam splitter; BPD- balanced photodetector pump and signal for picosecond pulse-pumped OPCPA in ALLEGRA [19]; however, the electronic feedback loop for our FSYNC system will be analogue, not digital. The electronic feedback for the fine/fast optical locking loop will run in quasi-CW acquisition mode using analogue waveforms. The optical synchronization between two master oscillators is still in the development phase. However, we have some preliminary results which show that the conceptual design for the electronic feedback can compensate RMS fluctuations with high precision.

Two optical beamlines are needed to produce the final signal for the BOC (as shown in Fig. 2). The first beamline (referred to as the primary beam in Fig. 2) begins with one output of the Ti:Sapph oscillator. The primary beam from the oscillator first goes through an AOPDF, which allows full control over the spectral phase (pulse duration). Here the pulse from the Ti:Sapph oscillator is stretched to ~2.5 ps, and it is then used as a seed for 4 stages of OPCPA. After the 4<sup>th</sup> stage of OPCPA, the seed was amplified to about 5 mJ using 1 kHz pump laser. A fraction of the energy (~500 uJ) was picked off from the output of the ALLEGRA front-end and filtered so that the center wavelength was 850 nm and a FWHM of 40nm. The filtered beam was then sent to a chirped mirror compressor (CMP), which decreased the pulse length to approximately 60 fs. The compressed pulse then propagated through a barium borate (BBO) crystal to generate the second harmonic of the fundamental wavelength. To correlate the output of ALLEGRA and the master oscillator, we decided to exploit the second-order (X<sup>2</sup>) process of optical parametric amplification. About 20 uJ of blue light (425 nm center wavelength) was achieved at the output of the single BBO crystal, which then propagated through a short-pass (SP) filter before it was used as a pump for two stages of OPA in one type 1 BBO crystal and one type II BBO crystal respectively.

The signal for the two OPA stages is essentially the second output of the master oscillator (referred to as the auxiliary beam in Fig. 2). The auxiliary output first propagates through a spectral filter, where the bandwidth was cut to a FWHM of 40 nm around 700 nm wavelength. The second beamline includes a delay stage to overlap in time the 80 MHz signal with the 425 nm pump from branch 1. The OPA process between the blue pump (425 nm) and the red signal (700nm) generated an idler with a center wavelength of 1.08 um. The type 1 BBO crystal combined with the type II BBO crystal, were orientated such that each idler generated had relative orthogonal polarization states while the pump and seed waves had constant polarization states. The three waves (pump, signal, and idler) were separated from one another using dichroic mirrors and low pass (LP) filters. The two idler beams were separated by a polarizing beam splitter (PBS), and then sent to a balanced photodetector (BPD). The signal from the BPD is used for the input for the analogue electronic locking loop, which consists of many acquisition electronics, including a sample and hold, PID (Proportional, Integral, Derivative) controller, and a piezo amplifier. The voltage output from the piezo amplifier went to an actuator which was attached to a mirror in the auxiliary beamline of the BOC system. This completed the locking loop.

## Polarization Multiplexing for Coherent Combination

FSYNC will serve as a testing bed to investigate methods of high energy, ultra-fast coherent combination. The demonstration of coherent pulse combining will translate into the constructive interference of 2 (or more) amplified coherent light trains (or pulses) that have same spectra (or close to identical spectra) to create one single train with more power (energy) than what is possible in a single amplification stage. The important quantitative measurement for this experiment will be the final combination efficiency (how much energy constructively interferes versus the total energy incident in the final combination stage). Fig. 3 shows a general set-up for a coherent combination experiment.



Fig. 3. Schematic setup of coherent addition of ultrashort laser pulses.  $\Delta \phi$ - element for path length matching [20]

Our version of Fig. 3 will be accomplished by seeding both the FSYNC and ALLEGRA OPCPA chains with one oscillator (Rainbow). The final output of both branches will be combined by constructively interfering the two amplified broadband pulses by stabilizing the path length and controlling the polarization at the final combining stage. The pilot research experiment has been done in a simplified scheme using relatively narrow-band pulses. We have preliminary results of splitting and combining the output of one of our thin disk pump lasers in the same configuration we hope to implement later once FSYNC is built. The following results are simply a proof-of-principle experiment. Fig. 4 shows the schematic of how we accomplished our first optical locking loop via polarization multiplexing.



Fig. 4. The scheme of the coherent combination locking loop testing. PBS – polarizing beamsplitter; NPBS – non-polarizing beamsplitter; PM – power/energy meter; BPD – balanced photodiode

Our preliminary coherent combination optical set-up was essentially a Mach-Zehnder interferometer, which was aligned with a laser beam with 1 mJ of energy, 1 kHz repetition rate, pulse duration of ~ 250 ps, bandwidth of 1nm FWHM, and electric field that is p-polarized. After the interferometer was carefully aligned, the energy of the laser was increased to almost 5 mJ of energy. The beam was incident on a half-wave plate so as to rotate the electric field by 45 degrees and then the single beam was split into two beams with equal path lengths via a polarizing beamsplitter (PBS). Both split beams recombine on a polarizing beam cube, after

which, depending on the delay between the two pulses on the recombination beamsplitter, the resulting polarization of the combined pulse can take any value of being elliptical/circular or being linearly polarized at  $\pm 45$  deg at the extremes. Mathematically, this combination process can be represented by the addition operation using Jones vector algebra [9]:

$$\mathbf{J}_1 = \begin{bmatrix} a \\ 0 \end{bmatrix} + \begin{bmatrix} 0 \\ b \end{bmatrix} \exp(i\Delta\varphi) = \begin{bmatrix} a \\ b \exp(i\Delta\varphi) \end{bmatrix}$$
(1)

Two pairs of power-balanced, orthogonally linearly polarized beams can thus produce two new orthogonally polarized beams at  $\pm 45$  deg (Fig. 5a); however, if the beams are not power balanced, the polarization vector of the output beam will be pointing in a different direction (Fig. 5b). Ultimately, the coherent beam combination typically requires the component beams to be power-balanced in order to produce the maximum efficiency [9].



Fig. 5. Jones vector representation of coherent superposition of two orthogonal polarization states (a) equal vector lengths and (b) unequal vector lengths [9]

In case of linear polarization, a second half-wave plate can be used to make it either vertical or horizontal. The combined beam is then split in a 10:90 non-polarizing beam splitter. The beam with ten percent of the total power is incident on a quarter-wave plate to rotate the electric field from linear to circular polarization. The circularly polarized beam is split by a PBS into equal parts and is used as a signal for the electronic feedback loop, which consists of a balanced photodetector, PID control and piezo actuator. The task of the feedback loop is to stabilize the paths and compensate for the occurring perturbations and to keep the polarization linear and constant. The beam with ninety percent of the total power is used to determine the combination efficiency by measuring the energy of the rejected (incoherently combined) beam and coherently combined beam power simultaneously.

#### SYNCHRONIZATION RESULTS

#### **RF** Locking

A phase noise analyser was used to determine the temporal jitter of each RF-locked oscillator and the pure RF reference, which are related mathematically to each other. These phase noise measurements were done with offset frequencies ranging from 1 Hz to 1 MHz. The jitter density of the "free running" oscillator can be calculated by subtracting the RMS jitter squared of the RF reference from the RMS jitter squared of the locked oscillator. We can then add each individual "free running" value in quadrature (assuming the jitter is uncorrelated) in order to obtain the highest value of jitter contribution from the ALLEGRA and FSYNC oscillators, which was calculated to be 98 fs RMS. This value represents the jitter that cannot be compensated solely with RF phase locking. To think about it from another perspective, we must compensate this noise using optical techniques in conjunction with phase locking. We cannot simply only utilize RF locking methods to obtain femtosecond synchronization.

#### **Balanced Optical Cross-Correlation**

In order to calculate the RMS fluctuations (standard deviation) of the locked and unlocked loop in fs, we first had to calculate the signal amplitude change of the unlocked analogue waveform as we applied a voltage sweep on the piezo actuator. After the calibration factor was calculated (25.8 fs = 100 mV), the RMS fluctuation of the analogue waveform could be converted from V to fs. The final RMS in fs is displayed in Fig. 6. For the portion of the graph where the PID loop is on, the RMS fluctuation (in the closed feedback loop) was 2 fs; for the portion of the graph where the PID loop is off, the RMS fluctuation (likewise, in the closed feedback loop) was 6 fs.



Fig. 6. Locked and unlocked analogue output waveform with PID loop on and off

In essence, we have completed and verified the fine/fast closed feedback loop, which stabilized the OPCPA compressed output with fs timing jitter relative to the oscillator output. We also confirmed that the electronic noise floor is ~100 times less than the noise floor on the acquired waveform by doing a frequency analysis of measured arbitrary waveforms in the Fourier domain. This noise measurement allowed us to confirm that our electronic feedback loop will be suitable for femtosecond synchronization and we will use this electronic set-up in our two-colour quasi-CW BOC for synchronizing the Origami and Rainbow oscillators.

#### **Polarization Multiplexing**

The goal of the pilot experiment using the method of polarization multiplexing was to demonstrate coherent combination of two beams with a combination efficiency greater than 90%. By using active phase control, coherent combination between two multipass thin-disk lasers was achieved with combination efficiencies ranging from 99% to 75%, depending on the configuration of their experiment [21]. By measuring the rejected beam energy and coherently combined beam power, we determined the average combination efficiency and the stability of the feedback loop when it was active (Fig. 7). For an average combined power of ~4.2 W (corresponding to 4.2 mJ), the resulting average combination efficiency was calculated to be ~ 94.8%. In order to be more thorough with our conclusions about the combination efficiency, the fast variations of the combination efficiency were calculated and are displayed in Fig. 8. One can see that while the feedback loop is engaged, the efficiency does not drop below 90%. Our time resolution of the calculation for fast variations in combining efficiency is limited by the sampling rate of the power meter, which was sampling data every second (the average energy of 1000 pulses). We have also calculated power noise spectrum of the rejected beam to understand numerically what noise frequencies contribute to incoherent beam combination. We are limited ultimately by the DC component of the noise. However, we do have substantial noise peaks at 100 Hz and its higher harmonics, which we think could be due to ambient scattered light. As we continue with our experimentation, we will move forward to suppress this. We plan to repeat this measurement for the broadband pulses.



Fig. 7. The measurement of the closed loop stability. The blue dots represent the energy in the rejected pulse channel (measured every pulse), and the red curve is the average power in the combined channel, measured by a thermal power meter.



Fig. 8. Coherent combination efficiency variations while the feedback loop is active for 600 seconds

## **CONCLUSION AND FUTURE PUMP-PROBE EXPERIMENTS**

In this paper, different ways of optical path stabilization have been addressed and how the relatively simple individual locking systems cooperate in tandem to synchronize a complex system like the FSYNC laser beamline to within femtosecond precision. It has been demonstrating that using the techniques described above, remotely located lasers and microwave sources can be synchronized with less than 10 fs precision over more than 10 hours [17]. Although we have achieved femtosecond synchronization using a combined technique of RF locking and BOC, our system must maintain this precision over several hours to be a practical system for user experiments. Long-term drift compensation will be an important issue to address once the optical beamline for FSYNC is fully completed. We would also like to explore the long-term stability of the coherent multiplexing interferometer. We plan on repeating our coherent combination experiment using broadband laser pulses from FSYNC and ALLEGRA systems with an active feedback loop that can compensate for short-term and long-term drift, while also maintaining a combination efficiency greater than 90%.

The understanding of ultrafast dynamics is contingent on highly synchronized excitations or perturbations in order to understand fundamental behaviour. When the FSYNC project is complete, it will vastly expand the number of physical processes that can be explored via pump-probe spectroscopy due to its ability to rapidly scan across different pump-probe delays over an enormous dynamic range. This will allow experimental groups to investigate inter-connected dynamics, covering the femtosecond to millisecond time scales, which are needed to reach an understanding of complex phenomena. One of the potential complex phenomena that could be explored in greater depth with FSYNC are Rhodopsins, which are light-sensing photoreceptor proteins, widely distributed in Eukaryota, Bacteria, and Archaea [22]. When excited with UV light, they have photoresponses ranging from times <100 fs to 58 µs after incident excitation [22]. Another example is the study retinal dynamics, which can be understood by the Raman and absorption spectrum of the sodium ion pump rhodopsin [23].

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## HIGH-THROUGHPUT LASER ABLATION AND POLISHING OF COPPER CYLINDERS

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#### ABSTRACT

The need for various microstructures in different materials is increasing rapidly. This need is successfully met by laser micromachining technology because it is a contactless, fast, and precise process that allows a wide range of materials to be used. However, the process cost is the major limiting factor. To use the laser irradiation most efficiently various laser parameters such as pulse repetition rate, pulse duration, fluence, pulse overlap, and others need to be optimized. It is of high interest to optimize this process because two-and-a-half-dimensional (2.5D) laser micromachining allows various bio-inspired functional surface structures to be mimicked on complex shaped surfaces. In this paper, experiments were carried out using an ultrafast laser with variable MHz repetition rate to find optimal pulse energy and repetition rate for the highest ablation efficiency to ablate cylindrical copper samples. Experimental results were compared to a well-known theoretical ablation efficiency coincide well with the best machining quality in terms of the smallest surface roughness with the mirror polishing finish. The optimal parameter set was used to laser machine drag-reducing blade riblets on the cylindrical copper samples.

**Keywords:** laser ablation, ablation efficiency, laser polishing, surface roughness, cylindrical samples, bio-inspired surface mimicking, copper

## **INTRODUCTION**

The need for microstructures on various materials is increasing rapidly because technology is constantly evolving. This need is successfully met by laser micromachining technology because it is a contactless, fast, and precise process that allows a wide range of materials to be used [1,2]. One of the most commonly used materials is copper. It is quite an inexpensive metal with sought-after qualities such as resistance to corrosion, and conductivity to heat and electricity. It is possible to cut, drill weld, mill and change the colour of copper using laser irradiation. More recent technologies allow for the two-and-a-half dimension (2.5D) and three-dimensional (3D) micromachining on metals [3]. This allows for bio-inspired structures to be made. Bio-inspired structures mimic structures found in nature, which allows certain properties to be achieved. For example, shark-skin-inspired blade riblets have drag-reducing and energy-saving properties in turbulent flow at solid-liquid/solid-gas interfaces [4]. However, while laser micromachining has many applications, the limiting factor is the process cost. Therefore, how to use laser irradiation effectively is an important question. A model predicting the optimal laser fluence for maximal laser ablation was presented by Furmanski et al. [5]. The model can be improved because the ablation rate depends on various laser parameters, such as fluence, pulse overlap, pulse duration, beam radius, and more. In this work, experiments were carried out using a MHz repetition rate laser to find the optimal pulse energy and repetition rate for the highest ablation efficiency. The experiments were done on a cylindrical surface using a complex 5-axis rotational system. The results were compared to a well-known theoretical model and small deviations were explained. Optimal parameters were used to machine blade-riblets on the cylindrical samples with very low surface roughness.

## MATERIALS AND METHODS

## **Experimental setup**

A laser source (Atlantic, Ekspla) with an average optical power of 50 W and a wavelength of 1064 nm was used for the experiments. The pulse duration was 10 ps and the maximum available repetition rate was 1138 kHz. The laser beam was focused using an F-theta lens with a focal distance of 160 mm. The sample was controlled inside a 5-axis rotational system (Duo MASTER, Elas). The beam was controlled in the x and y directions on the target's surface by a galvanometric scanner (Intelliscan 14, Scanlab). The sample was also rotated during the experiments in two planes: the yz rotational plane and xz tilt plane (ACS-15029-ES-17308-2, Aerotech). F-theta lens with the galvanometric scanner was moved in the z-direction by a z stage (PR0165-05MM-200-UF, Aerotech). The beam radius in the focal plane was measured using a well-known D squared method [6] and was equal to 18 µm. During the experiments, the ablated depth was kept well below the Rayleigh length so no beam focusing adjustments were needed during the ablation process. 0.1 mm length lines were scanned forward and backward in the x-direction (Fig. 1) on the sample. The sample was rotated at the same time in the vz plane as stated above. Multiple rotations were needed for the ablated depth to be easily measured using a stylus profiler. For the highest fluences 10 rotations were enough; however, for the lower fluences, between 40 and 125 rotations were used to achieve similar depth. The fluence was varied by reducing the maximum optical power of 50 W to 4 W by a step of 6 W. This was done using the internal laser attenuator. This was repeated several times using 404 kHz, 602 kHz, 808 kHz, and 1138 kHz repetition rates, which were restricted by the laser source. The pulse overlap was kept constant. Because the repetition rate was increased, the scanning speed was also increased to compensate. A pulse overlap of 95 % was chosen because it is the optimal value for the highest material removal rate [7].

For the laser texturing of shark-skin-like blade-riblets, a similar micromachining process was done. 20 mm lines were scanned from the front of the cylinder to the end and back to the front. Each line was 10  $\mu$ m further in the *y*-direction until the wanted width was achieved. This was repeated until a wanted depth was reached. Then the sample was rotated a certain number of degrees, depending on the width of the ablated groove and the process was repeated until the whole cylinder was micromachined. Using this method, it is possible to control the depth and width of the groove as well as the wall thickness.



Fig. 1. An experimental model of the ablation experiment

#### Sample characterization

Cylindrical copper samples with a purity 99.9 % were used. The diameter of the cylinder was 2 mm, and the length was 20 mm. A stylus profiler (Dektak 150, Veeco) was used to measure the depth of the ablated cavities, as well as the surface roughness  $R_a$ . A scanning electron microscope (SEM) (JSM-6490LV, Jeol) and optical profiler (S neox, Sensofar) were used for visualization purposes. The ablated volume was calculated from the diameter change of the ablated cylinder.

## **RESULTS AND DISCUSSION**

Ablation rate (1) and ablation efficiency (2) [8] were calculated from the experimental data. The ablation rate was calculated by dividing the ablated volume by the processing time, whereas the ablation efficiency was also divided by the average optical power. The theoretical model used is the ablation model by Furmanski et al. [5] and Račiukaitis et al [9]. It uses a simplified view on laser ablation that does not include reflections from the surfaces or the titled crater walls.

$$\frac{\mathrm{d}V}{\mathrm{d}t} = \frac{\delta P}{2F_0} \ln^2 \left(\frac{F_0}{F_{\mathrm{th}}}\right),\tag{1}$$

here dV – ablated volume, dt – processing time,  $\delta$  – effective energy penetration depth, P – average optical power,  $F_0$  – peak fluence,  $F_{\text{th}}$  – ablation threshold.

$$\frac{\mathrm{d}V}{\mathrm{d}E} = \frac{\delta}{2F_0} \ln^2 \left(\frac{F_0}{F_{\mathrm{th}}}\right). \tag{2}$$

where d*E* is laser energy dose.

The optimal ablation efficiency was reached in the 5  $J/cm^2 - 8 J/cm^2$  range with the highest value of 2.3  $\mu$ m<sup>3</sup>/ $\mu$ J at the fluence of 7 J/cm<sup>2</sup> and a repetition rate of 602 kHz (Fig. 11). At fluences lower than 10 J/cm<sup>2</sup> the results corresponded well with the theoretical ablation model. However, at higher fluences, some deviations were seen. A higher deviation from the theoretical model was seen at higher pulse repetition rates. Increasing the laser power does not increase the ablation efficiency indefinitely. There is a critical fluence where the ablation efficiency starts to drop. The fluence is lower for higher pulse repetition rates. The deviations from the theoretical model can be explained by several effects. The main one is particle shielding. Particle shielding can reflect, absorb and scatter laser irradiation [10]. With higher repetition rates the time interval between two pulses is shorter, therefore pulses interact with the ablated particle plume generated by the previous pulse. High laser power also plays a role by increasing the temperature of the sample. This leads to an uneven surface witch also increases the laser irradiation scattering [11]. The highest ablation interval corresponded to the highest surface quality in terms of relative surface roughness (Fig. 11) [11]. Relative surface roughness is calculated:  $R_r = R_a / D_a \times 100$  %. Where  $R_r$  is the relative roughness,  $R_a$  -cavity surface roughness,  $D_a$  – the ablated depth of the cavity. The average cavity depth was around 260  $\mu$ m and the average surface roughness was around 3.6 µm, however, in the optimal fluence region,  $R_{\rm a}$  was around 1.1 µm. It is important to note that efficiency and quality are optimized together.



Fig. 11. Ablation efficiency and relative roughness dependence on fluence. Red squares and blue circles – experimental data. Red lines – equation (2) fit

Optimal parameters for the highest ablation efficiency were used to micromachine bio-inspired blade-riblets on the copper samples. Using our experimental method, it is possible to control the thickness of the wall and the width and depth of the ablated groove (Fig. 3).



Fig. 3. Scanning electron microscope images of bio-inspired blade riblets structuring on cylindrical copper samples using optimal laser parameters of 602 kHz at 22 W. Wall thickness and groove depth and width can be changed. In this example, they are 10  $\mu$ m, 100  $\mu$ m, and 200  $\mu$ m respectively. The surface roughness 0.7  $\mu$ m

## CONCLUSIONS

Optimal parameters for laser ablation were found for laser irradiation with 1064 nm wavelength and 10 ps laser pulse duration. The highest ablation efficiency of  $2.3 \,\mu m^3/\mu J$  and ablation rate of  $3.5 \,mm^3/min$  was reached at a fluence of 7 J/cm<sup>2</sup>, average laser power of 22 W at a pulse repletion rate of 602 kHz. It was shown that the optimal fluence interval for the highest ablation efficiency corresponds to the best surface quality. A straightforward increase in laser power does not increase the ablation efficiency. There is a critical fluence where the ablation efficiency drops and it corresponds heavily to pulse repetition rate. For higher repetition rates, critical fluence was lower. Bio-inspired surface micromachining was demonstrated. Blade-riblets were made on a cylindrical surface allowing for three different processing parameters to be controlled.

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# **CONFERENCE PAPERS**

1

## **II.5.** Plasmonics and Nanophotonics

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## GENERATION OF GOLD AND SILVER NANOPARTICLES USING NANOSECOND LASER AND ANALYSIS OF THEIR PLASMONIC PROPERTIES

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#### ABSTRACT

Gold and silver nanoparticles are applied in a variety of technologies, including advanced catalysts, SERS, and components of optical and electronic devices whose properties depend on plasmonic vibrations. Gold and silver nanoparticles have intense colors, high surface area to volume ratio, high electrical conductivity, chemical stability, catalytic functions, etc. The optical properties of metal nanoparticles depend on the localized surface plasmon resonance (LSPR).

The choice of the method for the synthesis of precious metal nanoparticles is no less important as it determines the morphology, stability, and physicochemical properties. The main problem encountered during synthesis is the uniform and repetitive deposition of nanoparticles. The use of a laser helps to solve this problem. Unlike traditional methods, this process does not require chemical reagents and deposition of nanoparticles in solution. Thermal heating of a thin metal coating with a nanosecond pulsed laser can be performed immediately on the desired surface. This method has the advantages of accuracy, easy laser parameters control, a low impact on the surrounding areas, and the surface itself. With this method, nanoparticles can be deposited directly and fairly evenly on various substrates and can be easily replicated.

Here, the generation of gold and silver nanoparticles on a glass surface from the metal films using a nanosecond laser and the investigation of the morphology and plasmonic properties of the particles will be presented. Also, the difference between the generated nanoparticle size, dispersion, and optical properties of different metals will be compared and analyzed.

Keywords: nanoparticles, gold, silver, nanosecond laser, localized surface plasmon resonance

## **INTRODUCTION**

Due to the wide absorption band in the visible electromagnetic spectrum, precious metals such as gold and silver have attracted attention. Their nanoparticles have intense colors, high surface area to volume ratio, high electrical conductivity, chemical stability, catalytic functions, etc [1, 2]. The optical properties of metal nanoparticles depend on the localized surface plasmon resonance (LSPR). LSPR is a frequency generated by conductive electron oscillations caused by interactions with an electromagnetic wave. The electromagnetic wave induces the dipole of the nanoparticle, and the repulsive force of the particle tries to compensate with the resonant wavelength. Colour change is an indicator that localized plasmon resonance is apparent. The size, dispersion, shape, composition and other properties of nanoparticles affects LSPR differently [3]. Therefore, the choice of the method for the synthesis of precious metal nanoparticles is important because it determines the morphology, stability, and physicochemical properties. Nanoparticle synthesis methods are divided into: chemical (synthesis in solutions), physical (solutions are affected by physical means) and biological (organic chemistry) [4]. The main goal is the uniform and repetitive deposition of nanoparticles.

This study analyses gold and silver nanoparticles generated by thermal heating of a thin metal coating with a nanosecond pulsed laser. This method does not require chemical reagents and deposition of nanoparticles in solution. Nanoparticles can be deposited directly and fairly evenly on various substrates and can be easily replicated.

## METHODOLOGY

#### Preparation of gold and silver films

In this study we used borosilicat glass as a substrate. A sputter Q150T ES was used to prepare the gold layers. This method is based on the application of the potential difference between two electrodes in a vacuum chamber with an electric field. The inert gas in the chamber is ionized. A metal target (cathode) is bombarded with argon plasma. Ionized argon gas knocks a group of atoms out of the target and they settle on the desired surface [5]. The method is popular for its simplicity and does not require stabilizers.

#### Synthesis of gold and silver nanoparticles

Samples of 3 nm and 5 nm metal (gold or silver) films were used in this work. When the sample was exposed to the laser, a color change could be seen (the gold film turned pink and the silver film yellow). This change indicates the presence of nanoparticles. The change was most pronounced at 50 mW, 100 mm / s laser beam speed, 0.5 kHz frequency and 100  $\mu$ J energy. To generate nanoparticles, it is sufficient to heat film to the melting temperature, accordingly, the laser beam was moved away from the focal position, thus reducing the energy concentration at one point. The brightest in color and most uniform sample was at a distance of 12.9 cm from the lens with 10  $\mu$ m and 100  $\mu$ m hatch.

The generation of gold nanoparticles scheme using a nanosecond laser on a thin metal film (3 nm and 5 nm) is shown in Fig.1. First, we see a thin gold film on a borosilicate glass (Fig. 1. a). In part (b) of the scheme, the film is exposed to second-harmonic laser radiation. The heated film melts and stays in an unstable phase until energy travels from the electron subsystem to the grid. In part (c) of the figure, we observe hydrodynamic instability that occurs in the dissolved gold layer, resulting in the spontaneous organization of the substance into the droplets depicted in part (d). When the laser pulse stops, the droplets rapidly cool and thus nanoparticles are formed. This process is explained by the dewetting process: local fluctuations in the thickness of the coating occur, in which the surface remains uncovered. For this reason, the molten coating transforms into nanoparticles, which shrink into spherical nanoparticles due to Van der Waals attraction forces [2, 6].



Fig. 1. Nanoparticle generation scheme

#### **Spectral measurement**

The reflectance and transmittance spectra of gold and silver 3 nm and 5 nm coated nanoparticles were measured with a PHOTON RT UV-VIS-MWIR spectrophotometer. Nanoparticles of 3 nm and 5 nm films were measured with a hatch of 100  $\mu$ m and 10  $\mu$ m. The spectrophotometer measured the wavelength from 300 nm to 700 nm, the sampling step: 4 nm, and the slit size: 150  $\mu$ m.

## **RESULTS AND DISCUSSIONS**

#### Morphology of the formed nanoparticles

SEM photographs in Figure 2 (a - b) shows 3 nm and 5 nm silver films surface before laser exposure. It shows that surface morphology is dependent on the thickness of the film: 5 nm coating islets are larger and more fused with each other than 3 nm coating islets. Prior to laser exposure, the colors of the coatings correspond to the colors characteristic of the macromaterial. Gold is grayish-yellow and silver has a grayish-blue hue.

Surface of 3 nm and 5 nm films after laser exposure with a hatch of 100  $\mu$ m are shown in Figure 2 (c – d), and with a hatch of 10  $\mu$ m in Figure 2 (e – f). The scales of the depicted photos differ: in Figures (a) and (b) - 200 nm; (c), (d) and (e) - 300 nm, and (f) 500 nm. After thermal heating with laser radiation the gold films take on a pink color and the silver coating- yellow. Comparing the 3 nm films after laser radiation we observe that at 100  $\mu$ m are visible metal coating islands that did not form into nanoparticles. We can assume that with this hatch, there are places where the laser beam does not pass because the lines are too far apart. This is avoided by the denser (10  $\mu$ m) laser hatch shown in Figure 2 (e). The dispersion of particle sizes is higher in the more densely affected coating. This occurs because the laser beam overlaps and passes through the same place several times. Each time it passes through the already generated nanoparticles, it gradually grows as it melts and adheres to nearby particles. It can be assumed that the use of a 3 nm silver coating creates the smallest dispersion because the particles are smaller, and the thicker the coating, the greater the dispersion of nanoparticle sizes and the formation of larger particles.

SEM images of the 5 nm films of silver and gold after laser radiation (Fig. 3), shows that the dispersion and size of Ag nanoparticles are significantly bigger. It is important to note that the scales of the photos differ: (a) - 300 nm, (b) - 200 nm. Silver nanoparticles have an average size of 47.9 nm, while gold nanoparticles are ~ 4 times smaller — only 10 nm.



Fig. 2. SEM photographs of the silver coating with a film thickness of (a) 3 nm; b) 5 nm;
Films after laser radiation with a hatch of 100 μm: c) 3 nm; d) 5 nm;
Films after laser radiation with a hatch of 10 μm: e) 3 nm; f) 5 nm



Fig. 3. SEM images of the films (5nm) after laser radiation with indicated nanoparticle sizes. a) Ag film, b) Au film

#### Plasmonic properties of gold and silver nanoparticles

Localized surface plasmon resonance occurs in thin layers of precious metals exposed to laser radiation, which is observed in the transmittance spectrum. The difference in plasmon resonance between Au and Ag is due to the properties of the metal. Although silver has better plasmonic properties, gold is more stable, does not oxidize therefore is often used in plasmonic sensors.

Transmittance graphs of films before laser radiation are presented in Figure 4. The thinner films of both gold and silver (3 nm) have a higher transmittance. As we have seen in the SEM photographs (Fig. 2.), the nanoparticles are not formed and we do not see signs of localized plasmon resonance that are revealed in the graphs of the laser-generated nanoparticles.

Comparison of gold and silver nanoparticles are shown in Figure 5. From both the SEM photographs (Fig. 3.) and the graphs (Fig. 5.), we observe that although the film is of equal thickness, silver nanoparticles form larger than gold. From the graphs, we learn that the resonant wavelength of gold nanoparticles vary from ~524 nm to ~535 nm, and silver nanoparticles vary from ~414 nm to ~446 nm. These parts are responsible for the localized surface plasmon resonance caused by collective electron oscillations on the surface of nanoparticles, causing strong light absorption and scattering. It can also be seen in graphs that silver plasmon resonance occurs over a wider range of spectra, which occurs when there is a dispersion of particle sizes in the coating. The exact resonant wavelengths are shown in the table (Table 1).



Fig. 4. The transmittance of Ag and Au films before laser radiation dependent on the wavelength

Film thickness	3 nm			5 nm
Hatch	100 µm	10 µm	100 µm	10 µm
Ag	414 nm	428 nm	439 nm	446 nm
Au	524 nm	529 nm	534 nm	535 nm

Table 1. Resonant wavelengths of Ag and Au nanoparticles



Fig. 5. Dependence of Ag and Au films on wavelength

The transmittance graphs of the same precious metal but different film thicknesses with the same laser settings are compared (Figure 6.). From the graph Figure 6 (a - d) we see that the dispersion of nanoparticle sizes is much larger in the thicker films (5 nm) considering that graphs are wider and the localized surface plasmon resonance is stronger due to higher absorption. Thinner (3 nm) films are covered with more uniformly sized particles due to the narrower graphs and weaker LSPR due to low absorption. But Figure 6 (b and d) shows that the thin film, with denser hatch approaches the localised surface plasmon resonance intensity of the 5 nm film, while still maintaining more uniform particle dispersion.

Taking into account all the presented graphs, it should be noted that as the particle size increases, the plasmon resonance shifts towards the longer waves, thus enhancing the absorption and scattering of the radiation.



Fig. 6. Dependance of transmission on wavelength. a) Ag ND from 3 nm and 5 nm films with 100  $\mu$ m hatch b) Ag films from 3 nm and 5 nm with 10  $\mu$ m hatch c) Au ND from 3 nm and 5 nm films with 100  $\mu$ m hatch d) Au ND from 3 nm and 5 nm with 10  $\mu$ m hatch

## CONCLUSIONS

In conclusion, gold and silver nanoparticles with LSPR were generated by thermal heating of a thin metal coating with a nanosecond pulsed laser. With this method, nanoparticles were deposited directly and fairly evenly on glass substrates, it has the advantages of accuracy, easy laser parameters control, a low impact on the surrounding areas, and the surface itself. It was observed that the resonance wavelength of silver nanoparticles varies from ~414 nm to ~446 nm, and gold from ~524 nm to ~535 nm. Furthermore, it was shown that nanoparticle sizes depend on the thickness of the film and the hatch. The smaller hatch allows the formation of larger nanoparticles (~ 2 times larger for a film 3 nm thick and ~ 1.6 times for a film that is 5 nm thick). And when generating nanoparticles from the same thickness film, gold nanoparticles are formed ~ 4 times smaller than silver; the average diameter of the gold particles formed from the 5 nm coating was ~10 nm, and that of the silver ~47.9 nm. Lastly, it is important to mention, that as the nanoparticle size increases the localized surface plasmon resonance shifts toward the longer waves, thereby enhancing absorption and scattering.

## ACKNOWLEDGMENTS

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## FORMATION OF GOLD MICROBUMPS IN THIN GOLD FILMS USING FEMTOSECOND LASER

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#### ABSTRACT

Periodic microstructures of noble metals have unique optical properties one of which is surface plasmon resonance phenomena. Due to the effect of diffraction, surface plasmons are excited in the array of microstructures, when the resonant wavelength is absorbed. The aim was to form periodic gold bumps in a thin metal layer and to measure their plasmonic properties. The hollow metal microstructures were generated by single pulses of a femtosecond laser, using the direct laser writing method. In comparison with more popular lithography methods, direct writing allows forming larger arrays, not limited by the diameter of the beam. The fabricated grating demonstrates the hybrid lattice plasmon polaritons in the VIS-NIR range. The investigation of the resonance dependence on the grating period, the thickness of the gold layer, light polarization, and angle of incidence was made. To ensure the nature of excited plasmons, certain experimental values were compared with theoretical values, calculated by the model of the resonance wavelength in the diffraction grating. It was investigated that with different polarizations, different diffractive resonance modes were obtained. The wavelength of these modes depends on the angle of incidence of light. Not only diffractive but also another fixed coupled resonance was noticed at the wavelength of grating constant for higher angles of incidence. It was determined that with a decreasing grating period, the wavelength of resonance also decreased. Also, the absorption of resonant wavelength was stronger in thicker metal layers. When the theoretical modeled values were compared with experimental values of diffractive plasmons, it was found that the periodic array of bumps, created with a femtosecond laser, acted as one-dimensional grating, which occurred due to the non-uniform formation of bumps in both directions.

Keywords: Plasmonic microstructures, surface plasmon resonance, gold microbumps, femtosecond laser processing

## **INTRODUCTION**

Noble metals, such as gold or silver, and their microstructures at the moment are widely investigated due to their unique optical properties like surface-enhanced Raman scattering [1] and surface plasmon resonance [2]. The latter phenomena occurs either in the excitation of surface plasmon polaritons (SPP) or localized surface plasmon, when the resonant wavelength of radiation is absorbed. The SPP is surface wave in the metal-dielectric interface that consists of an electromagnetic wave in the dielectric bound with the collective oscillation of electrons in the metal [3]. These oscillations on the surface of gold are excited using glass prism, which is based on the total internal reflection, or creating periodic microstructures on the surface and taking advantage of diffraction [4]. The diffractively excited SPP is more attractive due to the absence of additional equipment like a prism.

The resonant wavelength of SPP has a high dependency on the microstructures and their morphology, therefore high accuracy and reproducibility is required for the method [3]. One of the efficient methods is laser processing. It was investigated that using only a single pulse of ultrafast femtosecond (fs) laser, complex microstructures can be fabricated on the surface of gold [5]. Depending on the laser pulse width, fluence, and metal thickness, different morphology structures are formed. The most frequent are so-called microbumps and nanoantennas [6]. The main mechanism of this formation is induced thermal stresses, which in

highly elastic gold lifts the irradiated layer and forms structure [7]. The less energy-requiring microbumps were chosen to fabricate in this work.

The formation of gold microbumps commonly is executed using interference lithography [yuan]. However, in this work direct laser writing (DLW) was used [8]. The idea is that the laser beam is directly focused onto the desired place of sample, in this situation – surface, and is processed by a single ultrashort shot. This method is more flexible and universal than commonly used photolithography due to the non-limited size of the array, uniform formation of bumps in all processed area, and mask-less process.

The idea of this work was to show an alternative efficient way to fabricate periodic microstructures on the surface of the metal and to show that this way generated microbumps exhibit good plasmonic properties in all periodic matrices.

## METHODOLOGY

The periodic grating was fabricated on a thin gold layer with 25 nm and 50 nm thickness. The layer was deposited using Quorum Q150T ES sputter coater, with a coating speed of 0,2 nm/s. Additional measurement of the thickness was not applied, thus the minimal error of  $\pm 2$  nm may be present.

The bumps were generated using DLW with Yb:KGW based fs-laser Pharos (Light Conversion), using its second harmonic (515 nm) and 300 fs pulse duration. The Mitutoyo M Plan Apo NIR 100x objective was used to focus the laser beam directly onto the surface of the thin gold layer, that the diameter of the beam at the focal spot was about 1  $\mu$ m. The power of the laser radiation was chosen such that the single pulse would not exceed the ablation threshold of gold but would be high enough to induce modification of the irradiated layer. Periodic structures were formed by translating a sample in a line and using a pulse picker for pulse-on-demand mode. By choosing the correct translation speed and pulse picker repetition rate, the desired period between shots could be made. The pulse repetition rate was selected to be 4 kHz and 5 kHz, according to which the speed of sample movement was calculated so that the period between adjacent bumps would be respectively 600 nm and 700 nm.

The reflectance spectra were measured for both *p*- and *s*-polarized light in the interval of wavelength from 400 nm to 1200 nm with a step of 4 nm. The angle of the incidence was chosen to be 8, 15 and 30 degrees.

The morphology of the microbumps was examined by scanning electron microscopy (SEM). The micrographs were used to determine an approximate diameter of the structures.

To ensure the nature of excited plasmons, the experimental values were compared with calculated theoretical values by the model of the resonance wavelength in the diffraction grating. To find the resonant wavelength, the following formula was used:

$$\lambda_{SPP,1D} = \frac{d}{m} \left( \pm \sqrt{\frac{\varepsilon_d \varepsilon_m}{\varepsilon_d + \varepsilon_m} - \sin^2 \theta} \right)$$
(1)

where d is the period between adjacent microbumps, m is diffraction order,  $\theta$  is the angle of incidence of the radiation,  $\varepsilon_m$  and  $\varepsilon_d$  – metal (gold) and surrounding medium (air) dielectric constants, respectively.
#### **RESULTS AND DISCUSSIONS**

#### Morphology of bumps

Practically microbump matrixes of  $3x3 \text{ mm}^2$  and  $5x5 \text{ mm}^2$  in size were generated and later characterized by SEM. Figure 1 shows the surface morphology from the top and at a  $45^{\circ}$ angle. The structures were quite similar, the average diameter of bump on 50 nm thickness gold was 400 nm with a standard deviation of 17,6 nm, while the average diameter on 25 nm thickness layer was 348 nm with a deviation of 15,4 nm. Using SEM micrographs made at an angle, the preliminary height of the bumps was measured. The height of protrusions on 50 nm and 25 nm gold layer is around 165 nm and 145 nm, respectively. The size of microstructures was not identical, because with such sharp focus, even the slightest fluctuation of laser energy or layer thickness impact the outcome of the morphology.

In the left side of Figure 1 the linear defects can be seen along the laser scanning line, where no bumps were fabricated. The main reason for these recurring shortcomings was that the laser and the sample stage were not correctly synchronized. Due to the same reason, the microstructures were not perfectly periodical in both directions. Bumps along the laser scanning line were arranged periodically, however adjacent bumps perpendicular to the scanning line were not as orderly and excel dislocations.



Fig. 1. SEM micrograph of microbumps array in 50 nm thickness gold at a sample tilt angle of 45° (left). Top-view of several microbumps (right)

#### Exhibited plasmon resonance

Samples mentioned before were characterized by spectrophotometer, measuring their reflectance spectra. Figure 2 shows the reflectance of the microbump array on 50 nm gold with a 700 nm period. There can be seen strong dips meaning that the radiation is absorbed and the SPP is excited. The fabricated gratings demonstrate the, so-called, hybrid lattice plasmon polaritons in the visible – near-infrared range. Both graphs of *s*- and *p*-polarized light were made when the electric field of radiation was perpendicular to the laser scanning direction. This was achieved by changing the azimuthal angle by 90°.



Fig. 2. Reflection spectra of microbump matrix with 700 nm period. Reflection of *p*-polarized light (left) and *s*-polarized light (right). Theoretical values as points

The *s*-polarized light achieved resonance at a single wavelength, which was close to the period of the array. With ascending incident angle, the resonant wavelength slightly shifted to the shorter wavelengths. In comparison, *p*-polarized light excited SPP not at one, but at two wavelengths, which with increasing incident angle, made significant shifts from the wavelength of the period to both sides – lower and higher wavelengths. The shift was much bigger than for *s*-polarization, thus this resonance has a high dependency on the angle.

Theoretical values, calculated by formula (1), are marked as points with the corresponding color in the same graphs. The calculated values are nearly the dips of resonance at a respective angle and experimental results of diffractive plasmons are in good agreement with the theoretical model. The model was made for one-dimensional (1D) grating thus the fabricated array also acts as 1D grating.

Similar measurements were made for an identical array, only with a 600 nm period. The results, which can be seen in Figure 3, are almost identical, except all values of resonance shifted by approximately 100 nm to smaller wavelengths. The *s*-polarized light gives one resonance while *p*-polarized light excites plasmons at two different wavelengths.



Fig. 3. Reflection spectra of microbump matrix with 600 nm period. Reflection of *p*-polarized light (left) and *s*-polarized light (right). Theoretical values as points

Also, the array of 700 nm period microbumps on 25 nm thickness gold was investigated. The results were almost the same as in Figure 2. The only difference was that the reflection in the thinner layer was lower, thus the resonance itself also was weaker. This can be explained that through a thicker layer more radiation is transmitted and less reflected from it.

#### CONCLUSIONS

The direct laser writing was successfully used to fabricate a periodic array of microbumps on a thin gold layer. It shows good reproducibility, thus the valuable grating of the required size can be easily produced. The fabricated arrays act as one-dimensional gratings and excite diffractive plasmons, which resonant wavelengths can be easily calculated by the theoretical model. The period between bumps has a strong influence on resonance and with the increasing period, the wavelength also increases. The *p*-polarized light excites SPP at two different wavelengths for the same angle, and with the increasing incident angle, the resonances move away from one another. The *s*-polarized light excited SPP at one wavelength that is close to period and with increasing incident angle shifts slightly. The thickness of the layer does not have a big impact on resonant wavelength and only affects the quality of the resonance.

#### ACKNOWLEDGMENTS

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# **CONFERENCE PAPERS**

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#### THE EFFECT OF SPECIFIC SOIL MICROORGANISMS ON SOIL QUALITY PARAMETERS AND ORGANIC MATTER CONTENT FOR CEREAL PRODUCTION

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#### ABSTRACT

Soil chemical, biological and physical properties play important role in soil quality and are related with increasing organic matter (OM), plant nutrient content and availability, soil microbiological activity. New generation of soil amendments with specific soil microorganisms are great interest worldwide. Field experiments were carried out in 2018-2019 in Institute of Agriculture, Lithuanian Research Centre for Agriculture and Forestry. The aim was to determine the effect of bio-products with *Trichoderma reesei*, *Acinetobacter calcoaceticus* and *Bacillus megaterium* on soil organic carbon (SOC), soil respiration and microbial biodiversity on loamy Cambisol. Under dry meteorological conditions, bio-products with *Trichoderma reesei*, *Acinetobacter calcoaceticus* and *Bacillus megaterium* caused increase in SOC content, C/N ratio, humic/fulvic acids ratio, soil respiration and microbial biodiversity. We concluded that use of mixture of three products: *Trichoderma reesei* + *Acinetobacter calcoaceticus* + *Bacillus megaterium* are the most promising bio-amendment under changing climate conditions.

**Keywords:** Soil organic carbon, plant growth promoting rhizobacteria, plant growth promoting fungi, microbial biodiversity

#### Abbreviations

SOC – soil organic carbon

PGPR – plant growth-promoting rhizobacteria

PGPF – plant growth-promoting fungi

AWCD - average well colour development

R-richness

#### **INTRODUCTION**

Soil is essentially a slow renewable resource with a high degree of degradation and a very low rate of regeneration[1]. Intensive agriculture leads to soil erosion, depletion of organic matter and other nutrients which results to permanent soil degradation and productivity losses[2]. To maintain optimal yields and less depletion of the soil, it is necessary to protect soil from losses of organic carbon and biodiversity, micronutrient imbalance, acidity, and salinity[3]. The input of exogenous organic matter, such as straw or livestock manure, can enrich soil with the necessary elements and retard soil organic matter (SOM) decomposition. Soil quality parameters can be determined by analysis of soil chemical, biological and physical properties together[2][3]. To determine soil quality indicators such as particulate organic matter, active C, total N, microbial biomass, biological activities, enzymes, soil pH, cation exchange capacity, salinity, bulk density, amino sugar, and soil aggregation should be known[2][4]. Soil microorganisms consists largely of primary decomposers that mineralize organic materials and release nutrients and energy for plants by enzyme-facilitated metabolic systems[2][4][5]. Plant growth and yield in natural environments depend on a many interaction between plant roots, bacteria and fungi[4][6]. In the sense of decomposition of organic residues microbial communities can be broken down into fungal and bacterial groups, and research indicates that these groups functioning differently in the decomposition process[7][8]. Bacterial decomposition pathways support high turnover rates of easily available substances, fungaldominated decomposition pathways are slower and includes complex organic materials[4][7][8]. For this day it is known that main plant-beneficial rhizosphere microorganisms are mycorrhiza, rhizobia bacteria, PGPR such as Pseudomonas spp., Bacillus spp. or Azospirillum spp., and PGPF such as Trichoderma spp. and non-pathogenic Fusarium spp. strains[5][8][9]. PGPR and PGPF colonize plant roots and are responsible of plant defence not only against various foliar pathogens but also leaf-feeding insects[8][9]. There is no literature concerning the influence and relationship of tillage with microorganisms. This study was aimed to determine the influence of specific soil microorganisms (PGPR and PGPF individually and in a complex) on SOC, soil respiration and biodiversity on loamy Cambisol under reduced tillage conditions.

#### MATERIALS AND METHODS

#### Site and soil description

The field experiments were conducted in 2018–2019 at the Institute of Agriculture, Lithuanian Research Centre for Agriculture and Forestry ( $55^{\circ}23'50''$  N and  $23^{\circ}51'40''$  E). The prevailing soil is *Endocalcari-Epihypogleyic Cambisol* (CMg-n-w-can). According to composition of soil aggregates - 52-54% sand (2,0–0,05 mm), 29–32% silt (0,05–0,002 mm) and 14–19% clay (<0,002 mm) - soil was loam. Research scheme and product applications described in Table 1. During 2018-2019 where were grown two crops: winter wheat (*Triticum aestivum* L.) cv. Ada and spring barley (*Hordeum vulgare* L.) cv. Luokė. A field experiment was set up in three replications. The gross plot size and net harvested area of each individual treatment was 30,0 and 22,0 m<sup>2</sup>, respectively.

#### Table 1. Research design

		Application of bioproducts		
Treatments	Abbreviations	After harvesting - for decomposition of organic residues	After germination BBCH12-15	
Control 1	K1	-	-	
Control 2	K2	ammonium nitrate	-	
Trichoderma reesei	TR	Trichoderma reesei		
Acinetobacter calcoaceticus	AC	-	Acinetobacter calcoaceticus	
Bacillus megaterium	BM	-	Bacillus megaterium	
Trichoderma reesei+Acinetobacter calcoaceticus+Bacillus megaterium	TR+AC+BM	Trichoderma reesei	Acinetobacter calcoaceticus+Bacillus megaterium	

\* Used doses: *Trichoderma reesei* – 100 mL/ha, *Bacillus megaterium* – 100 mL/ha, *Acinetobacter calcoaceticus* – 100 mL/ha, ammonium nitrate - 20 kg N/t residues.

#### Soil sampling and analysis

Total nitrogen (N<sub>tot</sub>) and total carbon (C<sub>tot</sub> for estimation of C/N ratio) were analysed by the dry combustion method using a CNS autoanalyser Vario EL III (Elementar Analysensystem GmbH, Germany)[10]. Closed chamber method was applied to quantify total (autotrophic + heterotrophic) soil surface net CO<sub>2</sub> exchange rate (NCER). CO<sub>2</sub> fluxes were measured five times during each crop growing season, each measuring was made between 10 a.m. and 12 a.m. using a portable infrared CO<sub>2</sub> analyser (IRGA) attached to a data logger (LcSRS-1000; ADC BioScientific Ltd, UK). In each treatment, the collar was inserted to 7.0 cm soil depth; the chamber hood was placed on the collar for 5 min. until results were recorded in the data logger. Measurements were made with three replications. Expression of soil surface net CO<sub>2</sub> exchange rate:

NCER=
$$u(-\Delta c)$$

(1)

Where u is molar flow of air per square metre of soil (mol  $m^{-2s-1}$ ) and  $\Delta c$  is difference in CO<sub>2</sub> concentration through soil hood, dilution corrected (µmol mol<sup>-1</sup>).

Humic acid fulvic acids were determined according "Agricultural Chemical Analysis, Method 5.4. Cabi Publishing, 2002", gravimetric and spectroscopic methods. Substrate utilization potential as average well colour development (AWCD) and R index of the soil microbial community were determined according to the community level physiological profiles method using Biolog EcoPlates[11].

#### Statistical analysis

The data were analyzed using software STATISTICA Base (version 6). One-way analysis of variance (ANOVA) was applied to evaluate the significance of differences between the means of the experimental data. The data were compared using Fisher's least significant difference (LSD) test at the probability levels P<0.05 and P<0.01.

#### **RESULTS AND DISCUSSION**

According to the SOC content, the soil of experimental fields could be classified as having low humus content. At the beginning of the experiment SOC ranged from 0,91 to 0,93%. During 2018 - 2019 seasons (Fig. 1) average SOC content was higher in all treatments with microorganisms, compared to K1 and K2. In 2018, the highest SOC concentration was in treatment 3 (*Trichoderma reesei*). It was 10 % higher than in K1 and 7,1% higher than in K2. In 2019 highest SOC was in treatment 5 (*Bacillus megaterium*), i.e., 7,5% higher compared with K1 and 6,2% compared to K2.



Fig. 1. Average soil organic carbon concentration data during 2018-2019 field experiment

#### C/N ratio

The decomposition intensity of organic matter is best determined by the C/N ratio. In 2018 period C/N ratio (Fig. 2) was 11,4% higher in treatment 6 with *Trichoderma reesei*, *Acinetobacter calcoaceticus*, *Bacillus megaterium* compared to K1 and 10,3% with K2. In 2019 period C/N ratio (Fig. 2) was highest in treatment 6 it was 4,7% higher than K1 and 7,3% than K2. An increased C/N ratio during experiment period means that the ratio of mineralization/humification processes has changed.



Fig. 2. Average C/N ratio during 2018-2019 field experiment

#### Humic / fulvic acid ratio

Soil humus, especially its stable fractions, is formed slowly, so this indicator does not fully reflect the humification processes of embedded organic matter. The high humus content and low humic/fulvic acid ratio indicate that this humus is not long-lasting and the humification processes in such soils are weak. Humic / fulvic acid ratio was detected in 2019. Highest HA/FA (Fig. 3) ratio was in treatment 6 (*Trichoderma reesei*, *Acinetobacter calcoaceticus*, *Bacillus megaterium*) – 106,1% higher than K1 and 94,3 % than K2.



Fig.3. Average humic/fulvic acid ratio in 2019

#### Soil surface net CO<sub>2</sub> exchange rate

During experiment period, the mean soil NCER (Fig. 4) was highest in treatment 6 (*Trichoderma reesei* + *Acinetobacter calcoaceticus* + *Bacillus megaterium*). In 2018, in this treatment, the NCER was higher by 26,3%, compared to both K1 and K2. In 2019, the mean NCER was 23,4% higher than in K1 and 33,3% higher than in K2.



Fig.4. Average soil net CO<sub>2</sub> exchange rate

To compare the strategy of substrate consumption by the soil microbiomes, the matters contained in a Biolog EcoPlate were classified into 6 main groups: carbohydrates, carboxylic acids, polymers, amino acids, amines, amides and miscellaneous. Data revealed that in both dry experimental years dominated carboxylic acids. In 2018 they consist 28-32%, in 2019 - 28-31% from all substrate C sources (Fig. 5 and 6). Carbohydrates amounted 21-23% and 25-28%, amino acids 19-20% and 17-20%, polymers 14-16%, amines 4-6% and 4-5%, and miscellaneous 8% and 5-8%, respectively.



Fig.5. Level of consumption of substrates by microbial communities of soil, in 2018

In first dry year, influence of soil microbiological amendments on C sources of soil substrate was insignificant (Fig. 5). In next dry year, all products caused significantly higher optical density (OD) values of each substrate category, compared to both controls. Most significant effect revealed combined application in treatment 6 (*Trichoderma reesei*, *Acinetobacter calcoaceticus*, *Bacillus megaterium*) (Fig 6). The high level of carbohydrates and carboxylic acids substrate consumption is probably connected with the complexity of these substrates chemical structure and they require less time for decomposition.





Principle Components Analysis (PCA) of average well colour development (AWCD) data revealed that during the first 4 days of the investigation average well colour development (AWCD) has grown in all samples selected and this index shows that microbial community metabolic activity in relation to carbon substrates under analysis is high. In 2018, in the 4<sup>th</sup> day of incubation, the highest AWCD index was found in treatment 6 (*Trichoderma reesei*, *Acinetobacter calcoaceticus*, *Bacillus megaterium*) – it was 21-22% higher than in K1 and K2. Meanwhile, difference from controls K1 and K2 in treatments 3-5 amounted only 3-8%. In 2019, in the 4<sup>th</sup> day of incubation, the highest AWCD index also was found in treatment 6 (*Trichoderma reesei*, *Acinetobacter calcoaceticus*, *Bacillus Megaterius*) – it was 22-28%

higher than in K1 and K2 treatments. Difference from controls K1 and K2 in treatments 3-5 reached only 8-13% (Fig. 7).



Fig.7. Influence of microbiological amendments on AWCD

The richness (R) index showed that the microbial diversity varied with the type of soil management and generally increased with the combined application of microbiological products TR+AC+BM (Fig. 8). Microbial richness varied significantly (P < 0.05) in both experimental years. In 2018 the highest R value was determined in treatment 6 (*Trichoderma reesei*, *Acinetobacter calcoaceticus*, *Bacillus megaterium*) and it was 4-5% higher than in K1 and K2 treatments. Meanwhile, differences from controls K1 and K2 and treatments 3-5 were insignificant. In 2019 the highest R value was determined in treatments 4 (*Acinetobacter calcoaceticus*) and 6 (*Trichoderma reesei*, *Acinetobacter calcoaceticus*, *Bacillus megaterium*). R index was 6-7% and 7-8% higher, respectively, than in K1 and K2. The correlation between AWCD and R indices was very high (r= 0,91-0,95). The increase in values of ACWD and R is likely related with SOC increase.



Fig. 8. Influence of microbiological amendments on soil R index

Climate change, production intensification conditioned great changes of soil environment. Therefore worldwide is increased interest in application of microbial amendments that provide natural benefit for soil and crops. Under commercial field conditions, microbial amendments can play an important role for environment and human health also[12].

Securing and improving soil quality is a central challenge in face of climate change. Considering the importance of micro-biota for soil ecosystem the exploitation of microbial activity could provide means to achieve soil improving. The application of microbial amendments could improve use of plant nutrients, reduce their release into soil and water and consequently reduce the negative effects on the environment[13].

Our results obtained are in line with other published data. We found positive effects of microbiological soil amendments on Cambisol properties. Bio-products with *Trichoderma reesei, Acinetobacter calcoaceticus* and *Bacillus megaterium* caused increase in SOC content, C/N ratio, Humic/Fulvic acids ratio and improved soil vitality by increasing soil respiration. We suppose that such results were governed by changes in soil physical properties. Pore structure, soil aggregate stability and water retention are under investigation in our experiment. Similar results were reported from sodic soils[14].

Bio-products act through a complex mechanisms including plant roots, nitrogen fixation, P-solubilization, etc[15]. Therefore we think that microbiological product of new generation can be advantageous under intensive farming conditions in commercial agriculture.

#### CONCLUSION

1. Under drought conditions, bio-products with *Trichoderma reesei*, *Acinetobacter calcoaceticus* and *Bacillus megaterium* caused increase in SOC content, C/N ratio, Humic/Fulvic acids ratio.

2. All tested bio-products increased soil respiration. The highest respiration was observed in soil after application with mixture of three products: *Trichoderma reesei* + *Acinetobacter calcoaceticus* + *Bacillus megaterium*. It was 23,7-26,5% higher, compared to soil respiration in crop growing technologies without bio-products.

3. The highest AWCD index and R index was found in treatment after application with mixture of three products: *Trichoderma reesei* + *Acinetobacter calcoaceticus* + *Bacillus megaterium*.

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#### INFLUENCE OF HIGH-DENSITY PLANTING FOR CV. AUKSIS WITH SUPER-DWARF ROOTSTOCK P 22

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#### ABSTRACT

Apples (*Malus* domestica) both fresh fruits and their products are widely used in the world. Horticulture is also adapting to the growing demand for food in the world. High-density planting schemes are used to obtain higher yields from a smaller unit area. The aim of this study was to analyze the impact of high-density planting schemes on apple trees physiology and fruit quality at harvest time. Apple tree cultivar 'Auksis' was grafted on super dwarfing P 22 rootstock and planted at distances from 0,25 m to 1 m in rows, while space between rows was 3 m. The experiment was carried out in 2017-2019 in Lithuania (55°60'N, 23°48'E). Leaf and fruit samples were taken from the whole apple canopy during harvest time at BBCH 87-88. Increased apple tree density resulted the significant increase of the average leaf area, while the most intensive accumulation of dry mass in the leaves and fruits were found in apple trees planted at 3x0.75m distances. Increased density up to four times from 1m to 0.25m between trees, reduced the fruit yield from the tree to 53%, while the yield per unit area increased to 88%. After evaluating the obtained results, the most optimal planting scheme for apples cv. Auksis grafted on super dwarf rootstock P22 is 0.75m between apple trees. Such distance results the higher yields with higher dry mass content without losing the overall quality of the fruits.

Keywords: apple, dry mass, hight-density planting

#### **INTRODUCTION**

As the population of the land grows and the agricultural land shrinks, new challenges arise for agriculture to provide food for humanity. High-density planting schemes used in horticulture help to reach a fully covered land surface faster and get a higher yield from the area earlier than conventional orchards [1,2]. After banana, apple (*Malus domestica*) is one of the most cultivated fruit species which is considered as a sun plant which means, that they need lot of sunlight [3,4]. As the planting density increases, the trees shade each other more intensely which contributes to the decrease in photosynthetic efficiency [5]. With sufficient sunlight, photosynthetic processes take place efficiently, during which various metabolites are formed. A decrease in the rate of photosynthesis also leads to a decrease in biomass. In general, biomass productivity depends on the optimal operation of the plant photosynthesis system and nutrient supply [5,6]. Studies show that shading trees by a quarter did not significantly influence plant height or root and leaf dry weights, however 75% shading resulted in a decrease in root and leaf dry weights compared with the non shaded trees [7,8,9].

During photosynthesis processes, the metabolites produced in the leaves are transported not only to the entire nutrient supply of the plant but also to the fruit [10,11, 12]. Disorders of photosynthesis and a decrease in the amount of dry mass in the leaves also reduce their transport to the fruit [12]. Apple cv. Auksis grafted into P 60 rootstock results show that increased density of apple trees significantly reduced the total sugar content of the fruit, which leads to lower fruit sweetness but no significant impact on dry mass was found [2]. Still, not only sugar content but

also acidity is important for the overall taste and quality of the fruit. The main organic acid in apples is malic acid, and its content is often used to describe the total acidity of apple fruits [13,14].

In addition to all other important components, apples also contain chloroplastic pigments and carotenoids, which accumulate mainly in the peel of the apple [15, 16]. Chlorophylls and carotenoids are lipophilic compounds that are synthesized and accumulate in plant cells. The green color of unripe apples is determined by the total occurrence of chlorophylls and carotenoids, and as the ratio of carotenoids and chlorophylls changes during ripening, the color of ripe fruit is mainly determined by carotenoids [17].

A review of research in this topic reveals a lack of systematic information on the impact of high-density planting schemes on both apple tree physiological response, fruit quality and their interactions. Therefore the aim of this study was to analyze the impact of high-density planting schemes on apple tree cv. Auksis grafted on super dwarfing P22 rootstock physiological response and fruit quality at harvest time.

#### **MATERIALS AND METHODS**

#### Plant material and growing conditions

A field experiment was carried out in an intensive apple orchard (Lithuania, lat.  $55^{\circ}$ N). The apple tree (*Malus domestica* Borkh.) cv. Auksis was grafted on super-dwarfing P22 rootstock. Apple trees were planted in rows of 3 m, maintaining distances in rows of 0,25 m, 0,5 m, 0,75 m and 1 m. Soil conditions of the experimental orchard were as follows: clay loam, pH 7.3, humus 2.8%, P<sub>2</sub>O<sub>5</sub> 255 mg kg<sup>-1</sup>, K<sub>2</sub>O 230 mg kg<sup>-1</sup>. Experimental variants are planted by the method of complete randomisation in three replicates, three trees randomized in each replication. Samples were taken at the harvest time BBCH 87-88 on September.

#### **Biometrical and biochemical analyses**

Determinations of dry mass in leaves and fruits. Twenty leaves were randomly sampled from all tree canopy and measured with a leaf area meter (AT Delta – T Device, UK) for the average leaf area (cm<sup>2</sup>). The dry mass of twenty leaves and five apples was determined by drying them in +70°C for 48 h. (Venti cell 222, Medcenter Einrichtungen, Gräfeling, Germany) to constant weight.

The chlorophyll and carotenoids determination in apple fruit peel. The 200 mg of fresh apple fruit peel were ground in ethanol for chlorophyll a and b (chl. a and b) and carotenoid analysis. The content of carotenoids and chlorophylls a and b (mg g-1) was evaluated spectrometrically using the Synergy HT Multi-Mode Microplate Reader (BioTek Instruments, Inc, Germany) at 441-, 662- and 644-nm wavelengths (D), respectively. All analyses were performed in triplicate. For the calculation of pigment content, the following formulas were used (Wettstein 1957):

$$chl a = 9.784 \times D_{662} - 0.990 \times D_{644} \frac{c \times V}{P \times 1000}$$
(1)

chlb = 21.426 × 
$$D_{644}$$
 - 4.650 ×  $D_{662}$   $\frac{c \times V}{P \times 1000}$  (2)

Carotenoid = 
$$4.695 \times D_{440.5} - 0.268 \times (\text{chl}a + b) \frac{c \times V}{P \times 1000}$$
 (3)

where c is the pigment content (mg g-1), V is the extract volume (ml), and P is the fresh mass of fruit peel (g).

Determination of malic acid by high-performance liquid chromatography HPLC. The content of malic was determined using HPLC, according to Wang et al. (2014) method on Shimadzu 10A (Japan) system with diode-array detector (DAD). Samples were prepared grinding plant material and diluting with H<sub>2</sub>0 1:10 (w:v). Extraction was performed in heated water bath (+50 °C) for 30 min. Extract was centrifugated at 10,000 rpm for 15 min and filtered through 0,22  $\mu$ m PTPE syringe filter (VWR International, USA). Separation was performed on Lichrosorb RP-184.6 × 250 mm, 5 5  $\mu$ m column (Altech). Mobile phase – 0,05 M sulphuric acid, flow rate 0.5 ml min<sup>-1</sup>, injection volume – 10  $\mu$ l. Calibration method was used for malic acid quantification (mg g<sup>-1</sup> in FW).

#### Meteorological conditions.

The meteorological data were collected from 'iMetos' meteorological station at Institute of Horticulture, LAMMC, Lithuania. During the vegetation period, the mean temperature was close to perennial for all three years of the experiment. Meanwhile, precipitation was irregular, rainy during fruit ripening, 125,4 mm of precipitation was in 2017, 86,2 mm in 2018, 207,2 mm of precipition in 2019 during fruit rippening in August. Perennial precipitation in August, during the fruit ripening period was 76 mm. Throughout the study year, the mean temperature was close to the perennial temperature during the vegetation period.

#### **Statistical analysis**

MS Excel Version 2010 and XLStat 2020 Data Analysis and Statistical Solution for Microsoft Excel (Addinsoft, France) statistical software were used for data processing. Analysis of variance (ANOVA) was carried out along with Turkey multiple comparisons test for statistical analyses,  $p \le 0.05$  (n = 9, 3 years, 3 repetitions each). Multivariate principal component analysis (PCA) was performed. The results are presented in PCA scatter plot that indicate distinct levels according to all analyses performed.

#### RESULTS

The increased density of trees resulted the significant increase of the average leaf area, significant differences were observed by reducing the distances to 0.5 m and less between trees in rows (Fig. 1). In contrast to leaf area, the increased density resulted the decreased percentage of dry mass. There was no significant differences for dry mass accumulation, however, 0.25 m resulted the decrease of 3.3% compared to 0.75m.



Figure 18. Influence of planting density on the average leaf area (A) and dry mass (DM) of the leaves (B). The average of three-year is presented, the error bars show standard deviation.

The different letters identify significant differences according to the Tukey test (p=0,05)

Reduced the distances between the apple trees from 1 m till 0.25 m resulted the reduced yield per tree up to 53% but the yield per hectare increased to 88% (Fig. 2A, B). However, the highest amounts of dry mass were accumulated at 0.75 m distances. While increased density (0.50 m and 0.25 m) decreased dry mass up to 8 -14% and decreased the distances the dry mass content decreases up to 13% (Fig. 2 C).



Figure 2. Influence of planting density on the yield per tree (A), yield per hectare (B) and dry mass (DM) of the apple fruit (C). The average of three-year is presented, the error bars show standart deviation. The different letters identify significant differences according to the Tukey test (p=0,05)

Apple fruit peel contained mainly chlorophyll b  $(0,11 - 0,19\text{mg g}^{-1})$ , followed by chlorophyll a  $(0,6 - 0,1 \text{ mg g}^{-1})$  and carotenoids  $(0,007 - 0,017 \text{ mg g}^{-1})$  (Fig. 3). The amounts of all three pigments increased significantly up to 55 – 70% at the distance of 3x0.75 m compared with other distances.





Malic acid is the main organic acid in apple fruits, the amount found in cv. Auksis apples ranged from 4.4 to 4.6 mg g<sup>-1</sup>. Planting density had no significant effect on malic acid content in fruits (Fig. 4)



Figure 4. Influence of planting density on malic acid in apple. The average of three-year is given, the error bars show standart deviation. The different letters identify significant differences according to the Tukey test (p=0,05)

The correlation circle showed the strong positive relationship between dry mass in leaves and fruits, the increased dry mass content in leaves followed the increased DM accumulation in fruits, while a strong negative relationship was found between yield from tree and yield from planting area (Fig. 5).

PCA results show the average coordinates of individual average leaf area, yield, dry mass of apple and leaves, chlorophyls a and b and cartotenoids in apple peel and malic acid in apple in response to different distances between trees. The first two factors (F1 vs. F2) of the PCA, as shown in the scatterplot (Fig. 5), explained 81.78 % of the total data variance. F1 explained 19.91% of the total variance, whereas F2 explained 61.88% of the total variability. The PCA scatterplot show significant differences between planting distances. The physiological response to 3x1.00 and 3x0.75 distances was significantly different from 3x0.5 and 3x.025..



Figure 5. The principal components analysis (PCA) and the PCA scatterplot, indicating distinct differences in leaf area, yield, dry mass of fruits and leaves, chlorophyls a and b and cartotenoids in fruit peel and malic acid in fruits.

#### DISCUSION

Increased density of trees reduced light penetration into the canopy and created competitive strees not only for light but also for water and nutrients. As our other studies showed, increased density between fruit trees significantly decreased the photosynthetic rate and other photosynthetic parameters, also, it affected metabolic processes, decreased the production and accumulation of photosynthetic metabolites [5]. The decreased light penetration through the canopy, resulted the bigger leaf area, because the plant tries to absorb as much sunlight as possible (Fig. 1). The plant shading reduced dry mass acumulation as well [20, 21]. Our results is in agreement with other authors who show that canopies with denser pruning form larger leaves and longer branches [2, 21].

In order to obtain a higher yield from the area, more intensive pruning and denser planting schemes is usually used. Apple trees grown in high-density orchards are more intensively pruned, they form smaller and thiner canopies. Thus reducing the yield from the tree, but this increases the yield per unit area [2, 22, 23]. Our results confirmed that increased density

decreased the yield from the tree, but increased yield from the unit area in cv Auksis grafted on dwarf P 22 rootstock (Fig. 2).

However, high yields are no longer the main goal at the moment, the must distinguish in high quality. The thendency of planting distances on dry mass accumulation was the same in the leaves and fruits (Fig. 1 and 2). The increased density between apple trees also affected the quality of the fruit. First of all, when the penetration of the sun into the canopy decreasesd the color of the fruit deteriorate [2, 24, 25, 26]. Our study showed that the highest pigment contents in the peel of the fruits was at 3x0.75 m planting distance, but further reduced distances between gtrees decreased not only carotenoids content, which disinguish in red and yellow color, but also chlorophyll a and b accumulation (Fig. 3).

Still,not only the composition but also the taste of the whole apple is important to the consumer. Much of the taste depends on the acidity of the apple and it is mainly determined by the malic acid [14, 27]. Some reseach states that a denser canopy increases the acidity of the apples [22], however not always a denser canopy increases the amount of malic acid in apples [27]. Using high-density planting systems for cv. Auksis grafted on superdwarf P 22 rootstock, even the reduced distances to 0.25 m between trees in rows did not change the amount of malic acid significantly (Fig. 4).

#### CONCLUSIONS

Summarizing the obtained results, we can state that increased density between trees reduced the yield from tree up to 53% but significantly higer yield per hectare (to 88%) was obtained. However, to achieve the best quality apple fruits, it is recommended to keep a distance of 3x0.75 m. for cv. Auksis grafted on superdwarf P 22 rootstock.

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#### AEROBIC PROCESSES EFFECT ON PERENNIAL GRASSES SILAGE SEALED USING VACUUM-PACKING

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#### ABSTRACT

Feed is the production potential of livestock products, which plays a significant role in shaping the quality and safety of the food chain. As soon as silage is exposed to air on opening the silo or during the feed-out, fermentation acids and other substrates are oxidized by aerobic bacteria, yeasts and molds. The aerobic stability of silage is a major factor in ensuring that silage provides wellpreserved nurients to the animal. This study aimed to assess aerobic stability in laboratory scale vacuum sealed perennial grassess silage. A mixture of perennial ryegrass, fescue and timothy grass was ensiled using Lactobacillus plantarum and L. pediococcus acidilactici additives, sealed using a vacuum sealer and stored for 90 days. Aerobic phase was observed for 30 days after initial opening. Temperature was beeing measured throughout the whole ensiling and aerobic spoilage process. Samples were taken immediately after opening silage and during the aerobic stage. Qualitative and fermentation quality indicators have been established using near infrared spectroscopy (NIRS-6500 (FOSS). Results showed that during ensiling crude protein (CP) and water-soluble carbohydrate (WSC) content decreased. Neutral detergent (NDF) and acid detergent fiber (ADF) content also decreased significantly. Throughout 30 days of aerobic stage neutral detergent fiber and acid detergent fiber decreased (NDF from 49.87% to 48.90%, ADF from 30.57% to 30.10%), while dry matter content (DM) increased from 50.29% to 56.36%. Organic acids didn't show any significant silage quality changes.

Keywords: Silage, Silage fermentation, Aerobic stability, NIRS spectrometry.

#### **INTRODUCTION**

Today, it is progressively important to save energy in the food production chain. The world's population is growing and the challenge of feeding people requires effectiveness in every step of food production [1]. The aims of feed conservation are maintaining quality and feeding properties of the fresh crop, and reducing dry matter and energy losses to a minimum [2]. During the intervening period, the ensiled crop depends on four phases: (i) the aerobic phase in the silo promptly after harvest, (ii) the fermentation phase, (iii) the storage phase in the silo and (iv) the feed-out phase when the silo is open and the material is in contact with air immediately before, during, and after its removal from the silo [3].

It is now acknowledged that the changes during the fourth or feed-out phase are equally important as those in the first two phases from the angle of preserving nutrients and maintaining good hygienic quality to the point of silage consumption by the animal [4]. The aerobic deterioration of silage is a worldwide problem for feed quality and farm profitability [5]. When silage deteriorates because of exposure to air, its nutritional value is reduced due to loss of fermentation products that are likely digestible substrates [6]. Animal health and quality of milk may also be affected negatively as a result of the growth of undesirable microbial spores [7].

Lactic acid, acetic acid, and water-soluble carbohydrates are the main sources of energy for the microorganisms involved in the first phase of silage deterioration [8]. The oxidation of these nutrients results in the production of carbon dioxide and water, with the development of heat and an increase in silage pH [9]. On the farm, this deterioration is usually apparent as an

increase in temperature and as the appearance of molds in the peripheral areas of the silo [10]. Nevertheless there is little data on tracking core temperature in vacuum-sealed silage.

Cai *et al.* [11] [12] reported the use of plastic bags sealed with a household vacuum sealer, however experimental details were not provided. A model system for laboratory-scale silage fermentations was investigated by Johnson *et al.* [13], yet the experiment did not provide insights on aerobic deterioration stage.

The objectives of this study were to determine: (i) the aerobic exposure effect on vacuum-sealed perennial grasses silage quality; (ii) evaluate silage core temperature in bags, sealed with vacuum sealer during silage fermentation and (iii) throughout the aerobic exposure stage.

#### **MATERIALS AND METHODS**

#### **Ensiling process**

Experiment was carried out at the Lithuanian Research Centre for Agriculture and Forestry. Perennial grasses were obtained from a private dairy farm in Pakruojis, Lithuania (55.81 N, 23.77 E). Raw material consisted of perennial ryegrass, timothy and tall fescue. The grass was chopped into approximately 2 cm pieces using a crop chopper and mixed with silage additive, containing *Lactobacillus plantarum* and *L. pediococcus acidilactici* (100 000 CFU/g). After thorough mixing, the fresh material (FM) was ensiled in triplicate at approximately 1 kg (fresh weight) in polyethylene bags (28 cm x 40 cm, thickness of 100 and 130 µm, Status Innovations Co., Metlika, Slovenia) and sealed by using a vacuum packing machine. There were 15 bags in total (90 ensiling days × 3 replicates + 3 days of aerobic exposure × 3 replicates + 28 days of aerobic exposure × 3 replicates). Packed silages were kept in ambient temperature (20 - 22 °C) for 90 days before initial opening.

#### **Measuring temperature**

After bags were filled with fresh matter, a temperature sensor (Tempmate. ®-S1 Single-Use USB Data Logger, Heilbronn, Germany) was inserted in the middle of each bag, as presented in Fig 1. Three of those sensors were taken out after opening samples and the rest (12 sensors) were left during the aerobic stage.



Fig. 1. Schematic illustration of the experimental setup

#### **Chemical Analysis**

After 90 days of ensiling, all the bags were opened. Three bags were sampled for quality analyses and organic acids determination. Bag content was thoroughly mixed and a sample of ~25 g was taken. Dry matter (DM) content was determined by drying samples at 105 °C for 48 h in a forced-draft oven until the weight of the samples was stable. Crude protein, crude fibre, water - soluble carbohydrates and acid detergent fiber in silage were determined by near infrared spectroscopy (NIRS), using a NIRS-6500 device with a sample spinning module (Foss-Perstorp, USA), using wavelengths between 400 and 2500 nm in reflectance. For NIRS

determination, the samples were oven-dried at  $65 \pm 5$  °C temperature to a constant weight and grounded in an ultra-centrifugal mill ZM 200 (Retsch, Germany) to pass a 1 mm screen. Then dried samples were scanned in a set of three using cuvettes, and the acquired spectra were processed with equations used in the device (ADAS, UK). Neutral detergent fiber (NDF) was analyzed according to methods described by Van Soest et al. [14]. Crude ash content was as the mass left after sample incineration at 550 (±10) °C. The acidity (pH) was measured in water extract, in accordance with a potentiometric method, using a pH meter (Horiba, UK).

Organic acids were also determined by near infrared spectroscopy. Subsamples were taken from main silages samples before oven drying. Subsamples were scanned and the spectra was processed with equations for undried samples (VDLUFA laboratory, Germany).

#### **Fermentation Quality of the Silage**

After 90 days of ensiling a total of 12 bags were opened for aerobic stability test. Bags were stored at ambient temperature (20–25  $^{\circ}$ C). Three bags were sampled at 3, 7, 14 and 28 days for quality indicators and organic acids.

#### 2.4. Statistical analysis

Statistical analysis was conducted using packages from the software IBM SPSS Statistics 25. Significant differences between the samples were calculated using t-Test: Paired Two Sample for Means. The values with  $P \le 0.05$  were considered statistically significant. The correlation analysis was performed to examine the quantitative relationship between the investigated variables. The strength of the correlation was estimated according to the value of correlation coefficient R. Significance level was calculated with a regression analysis tool in Excel, data were significant when  $P \le 0.05$ . The data of nutritive values of silage were expressed as mean  $\pm$  standard error (*SE*).

#### **RESULTS AND DISCUSSION**

#### **Characteristics of Fresh Matter before Ensiling**

The chemical composition of perennial grasses fresh matter is shown in Table 1. The DM contents of FM was 49.83%, which was comparable with data reported by John Moran [15]. Crude protein content varied from 16.53% to 17.20%, matching other recent findings [16] according to chemical and NIRS analyses results. Crude fiber ranged from 27.60% to 29.69%, and NDF with mADF, respectively from 51.63% to 53.95% and from 27.23% to 31.93%. WSC varied from 11.84% to 12.3%, which was sufficient as WSC is important for silage fermentation and concentration greater than 5%DM is crucial for acceptable silage quality [17].

Quality indicators	Means					
DM, % of FM	49.83					
CP, % of DM	16.86					
CF, % of DM	28.64					
NDF, % of DM	52.79					
mADF, % of DM	29.58					
DMD, % of DM	60.03					
WSC, % of DM	12.07					

Table 1. Chemical composition of fresh matter before ensiling

DM, dry matter; CP, crude protein; CF, crude fiber; NDF, neutral detergent fiber; mADF, acid detergent fiber; DMD, dry matter digestion; WSC, water-soluble carbohydrate.

#### **Temperature of the Silage**

The results of the temperature measurements are graphically represented in Fig 2. After ensiling, core temperature slowly and steadily dropped from 20.2 °C to 16.9 °C just before opening. This kind of temperature is characteristic to silage core during storage phase [18], especially in small lab-scale silos, which is usually similar to ambient temperature or just a few degrees warmer [10]. After initial opening on October 9, in a period of a couple weeks, temperature dropped to 15.2 °C. It might be the result of lower, ambient temperature air flowing into the bag and due to a reasonably small amount of silage which cools down easier. Core temperature reached its peak (28.9 °C) in a month after bag opening. High temperature in silo is usual due to aerobic deterioration. Silage exposure to the air develops into the growth of lactate-assimilating yeasts, an increase in silage temperature and pH [10]. During the storage phase, silage temperature in the silo core was reported to range from 12 to 26°C in Italy [18]. Core temperature differed according to the amount of forage ensiled and the type of storage. Kung [10] reported core temperature of 32°C after 90 d in silage in Wisconsin. Silages can be found to be relatively hot (>38°C) even after 4 to 6 weeks or even more, especially if harvested dry (>40% DM) and poorly packed (Kung, 2011).



Aug. 9/ Aug. 21/ Sep. 01/ Sep. 12/ Sep Days of aerobic exposure

v. 20/ Dec. 01

Fig. 2. Core temperature in silage during storage and aerobic stage.

#### **Chemical Composition of the Silage**

Chemical composition of the silage did not show significant quality losses during storage. Water-soluble carbohydrates declined from 12.07% DM to 2.69% DM. Rapid losses of WSC is normal due to respiration of WSC by plant enzymes and fermentation by aerobic micro-organisms until anaerobic conditions are achieved [19]. The epiphytic lactic acid bacteria (LAB) ferment the water-soluble carbohydrates in the crop to lactic acid, and to a lesser extent

to acetic acid. On account of the production of these acids, usually the pH of the ensiled material decreases and spoilage micro-organisms are inhibited [20] [21].

As shown in Table 2, time of aerobic exposure had a mild effect on silage quality indicators. DM content remained almost steady, up to the last sampling and the span of aerobic exposure had a significant effect on it (R = 0.85, p = 0.0002) and DM content was 56.36% on day 28. DM quantity on the opening day of the silage and on the 28<sup>th</sup> day of the experiment shows statistically significant differences. Higher DM contents in silage treated with lactic acid bacteria (LAB) could be due to the inhibition of undesirebale microorganism metabolism of silage nutrients [22]. Also, silage got visibly drier throughout the 28 days period, as the amount of the silage in a bag was comparetively low, which might have caused the increase in dry matter.

Aerobic stage also had a notable effect on ADF (R = -0.47, p = 0.0087) and NDF (R =-0.66, p = 0.0008) content. ADF steadily decreased for a week, although the average got higher with the last sampling, the minimum value decreased from 30.40% to 30.00%. The ADF concentration refers to the cell wall portion of the forage. These portions consist of cellulose and lignin. The ADF values are important because they describe the ability of an animal to digest this forage. When ADF increases, it usually lessens the digestability of the forage [23]. NDF quantity varied a little within the 28 days period and slightly decreased in the end of the experiment (from 49.87% to 48.90%). Although other authors report that, in fact, respiration tipically increases neutral detergent fiber and acid detergent fiber [24]. NDF value refers to the total cell wall, composed of the ADF fraction plus hemicellulose. Neutral detergent fiber values are important in ration formulation as they show the amount of forage that the animal can consume. As the NDF percentages increase, the dry matter intake will usually decrease [25]. NDF content variation might happen due to volatile ammount of soluble constituents in the silage [26]. However, other authors report that concentrations of ADF and NDF were not affected by the span of aerobic exposure, which might occur because the study was based on corn and sorghum [26].

In this research aerobic stage did not have a significant effect on CP, WSC and CF. According to the chemical composition, silage did not deteriorate and was still suitable for feeding.

Itoma		Days of aerob	ic exposure		
Items	0	3	7	14	28
DM, %	$50.29^{a}\pm0.92$	$51.83^{a}\pm0.48$	$50.00^{a}\pm0.44$	$50.86^{a} \pm 1.33$	$56.36^{b} \pm 1.08$
MIN	48.87	51.30	49.30	49.20	55.00
MAX	52.00	52.80	50.80	53.50	58.50
CP, % of DM	$15.86^{a}\pm0.20$	$15.90^{a} \pm 0.26$	$16.46^{a}\pm0.03$	16.13 <sup>a</sup> ±0.13	$19.40^{a} \pm 3.70$
MIN	15.50	15.40	16.40	16.00	15.60
MAX	16.20	16.30	16.50	16.40	26.80
WSC, % of DM	2.69 <sup>a</sup> ±0.26	$2.72^{a}\pm0.12$	$2.85^{a}\pm0.14$	$2.83^{a}\pm0.03$	$2.90^{a}\pm0.18$
MIN	2.23	2.48	2.60	2.78	2.56
MAX	3.14	2.87	3.08	2.88	3.17
CF, % of DM	$26.70^{a}\pm0.66$	$27.20^{a}\pm0.15$	$26.16^{a}\pm0.07$	$26.16^{a}\pm0.38$	$26.85^{a}\pm0.05$
MIN	25.40	26.90	26.10	25.60	26.80
MAX	27.50	27.40	26.30	26.90	26.90
ADF, % of DM	30.57 <sup>b</sup> ±0.12	30.33 <sup>ab</sup> ±0.13	$29.83^{a}\pm0.07$	29.97 <sup>a</sup> ±0.30	30.10 <sup>ab</sup> ±0.06
MIN	30.40	30.20	29.70	29.40	30.00
MAX	30.80	30.60	29.90	30.40	30.20

Table 2. Chemical composition of the silages during the aerobic exposure stage

NDF, % of DM	49.87 <sup>ab</sup> ±0.63	50.13 <sup>b</sup> ±0.37	49.00 <sup>ab</sup> ±0.21	$48.40^{a}\pm0.76$	48.90 <sup>ab</sup> ±0.21
MIN	48.60	49.40	48.60	47.40	48.50
MAX	50.50	50.50	49.30	49.90	49.20

DM, dry matter; CP, crude protein; WSC, water-soluble carbohydrate; CF, crude fiber; ADF, acid detergent fiber; NDF, neutral detergent fiber; CA, crude ash. Note: different letters next to the results, show statistically significant differences.

#### **Fermentation Quality of the Silage**

Fermentative characteristics during aerobic exposure are shown in Table 3. Span of aerobic stage did not have a statistically significant effect on silage pH or organic acids (p > 0.05). The pH value remained above 4.47 during exposure.

Itoms		Days of aero	bic exposure		
nems	0	3	7	14	28
pH	4.60±0.00	4.53±0.03	$4.50 \pm 0.00$	$4.80 \pm 0.00$	$4.47 \pm 0.03$
LA, % of DM	$73.60{\pm}2.61$	77.13±1.64	73.63±0.65	$86.50 \pm 5.59$	$84.00 \pm 2.93$
AA, % of DM	$5.67 \pm 1.20$	$5.00 \pm 0.58$	$6.67 \pm 0.33$	$1.67 \pm 0.88$	$2.00{\pm}1.18$
BA. % of DM	2.33+0.33	1.10+0.49	$0.97 \pm 0.03$	$1.30 \pm 0.35$	$0.93 \pm 0.03$

Table 3. pH and organic acids content in silage during the period of aerobic exposure

LA, lactic acid; AA, acetic acid; BA, butyric acid.

#### CONCLUSIONS

During 28 days of aerobic exposure, perennial grass silages did not show strong signs of spoilage. Nevertheless, exposure had significant effect on DM, ADF and NDF, as DM content increased, while ADF and NDF slightly decreased. Silage core temperature stayed similar to ambient temperature during the fermentation and decreased after initial opening. Slowly increasing again, temperature reached its peak in a month after the bag opening. Aerobic exposure did not have a statistically significant effect on silage pH or organic acids content. More research using controlled trials is needed to further investigate aerobic exposure effect on silage using vacuum-sealing.

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#### ADOPTION OF INTEGRATED WEED MANAGEMENT IN SUSTAINABLE TILLAGE

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#### ABSTRACT

Modern cropping systems throughout the world are highly dependent on herbicides for weed control. Herbicide resistance threatens the sustainability of these cropping systems. Growers are being encouraged to adopt integrated weed management practices that place less reliance on herbicides to delay, if not prevent, further resistance development. The readily measured benefits of herbicides must be balanced against the risks imposed upon society, the environment, and the long-term sustainability of agricultural economies. Integrated weed management approaches are one means to achieve this balance. Integrated pest management is inevitable in a modern farming system. Sustainable tillage to reduce greenhouse gas emissions, increase the amount of organic matter in the soil is also very important. Besides, it is an excellent anti-erosion agent. However, tillage extensification often results in a greater influx of pests, an abundance of weeds, more plant protection products, and the ploughing is often replaced by glyphosate. To combine these two important technologies into one sustainable, environmentally friendly farming system, we need to look for additional measures to combine integrated pest management with sustainable tillage. One possible measure is the sowing of cover crops. Detailed research on weed biodiversity, germination dynamics, seed bank changes, using tillage technologies of different intensities - cover crops will allow us to evaluate the possibilities of integrated weed control in traditional and sustainable tillage practice. The obtained results would supplement previous knowledge and have significant practical benefits.

Keywords: Integrated weed control, extensive tillage, cover crops

#### **EXTENDED ABSTRACT**

#### Literature review and relevance of the topic

Integrated weed control has been poorly implemented, with little evidence of a concomitant reduction in herbicides [1]. Research on this topic has focused on how crop yields and weeds are affected by different factors: such as tillage, herbicide application times and rates, catch crops, and sowing patterns. The prevalence of specific weeds increases the risk of developing their resistance to herbicides [2]. It is essential to include alternative weed control methods, such as crop rotation, increasing crop competitiveness, etc. [3][4]. In recent years, crop rotations have become minimal and extensive tillage has become more common, leading to a significant spread and increase in monocotyledonous weed populations. The emergence of resistant weeds can also be influenced by glyphosate's annual use, which is often used as an alternative to plowing. On this basis, alternative ways to control weeds in crops need to be explored.

In modern crop production, sustainable tillage (shallow tillage or even direct sowing) is increasingly being chosen. Every year, technical companies look for ways to offer farmers the most modern technical solutions possible, reducing energy and labor costs. Sustainable tillage is essential to reduce greenhouse gas emissions and increase soil organic matter [5]. Sustainable tillage is economically beneficial and reduces soil erosion but often causes a larger influx of weeds and pests [6][7][8]. For this reason, more plant protection products are being used, and

the plough is often replaced by broad-spectrum systemic herbicides. Glyphosate is one of the most commonly used herbicides worldwide. Weeds have the ability to adapt very quickly to a changing environment [9]. Therefore, changing tillage practices can radically change the range of weeds and population dynamics. Tillage plays an important role in weed management. Eliminating tillage removes the main weed management tool and reduces the efficiency of others.

The introduction of cover crops into crop rotation is one of the possible measures to apply sustainable tillage and increase biodiversity while creating the conditions for weed control. Cover crop biomass is an important source of organic carbon and nitrogen. Growing cover crops prolong the positive effects on the soil. Many studies have examined the effects of cover crops on subsequent crop yields. The results varied widely depending on factors such as the type of the crop, the quantity and quality of biomass, environmental factors, and cultivation practices [10]. Cover crops can be plants that accumulate excess nitrogen from the soil (white mustard, radish, buckwheat) and plants that fix air nitrogen (annual clover, lentils, phacelia). Cover crops sown after the main crop in the winter fallow niche serve multiple purposes. They prevent soil erosion and nutrient leaching, especially if they are nitrogen scavengers. Cover crops can either be sown after harvest of a main crop, or they can be sown into a standing crop (over-seeding).

Weed control is an important technique to reduce crop yield losses and prevent the spread of weed seeds in order to reduce stocks of seeds in the soil. Most weed seeds entering the soil are matured seeds of annual weeds before harvest [11]. Analysis of weed seed quantity and seed bank provides information on past and present weeds and can help predict future weeds [12]. Changes in the amount of weed seeds in the soil also depend on tillage, crop rotation, and weed control measures [13][14][15]. Extensive research on weed biodiversity, germination dynamics, seed bank changes using different intensities of tillage-catch crops would allow us to assess the potential for integrated weed control, not only in traditional but also in sustainable tillage practices.

A significant role of weeds is in the spread of plant diseases. Weeds can serve as alternative hosts for Fusarium fungi without visual symptoms of the disease [16][17][18]. Researchers point out that plant residues on the soil surface contribute to a higher spread of the disease due to sustainable tillage [19]. An effective way to reduce fusarium head blight (FHB) in cereals is to use fungicides on time. The results of the research show that the cultivation of catch crops suppresses weeds and harms the causative agents of FHB in cereals [19]. For these reasons, it is essential further to explore possible alternative measures for integrated weed control, especially when using sustainable tillage. Although experiments have already been carried out on this topic, it is important to investigate which catch crops provide the greatest benefits for soil and biodiversity and are best suited to Lithuanian conditions.

The European Commission's ban on glyphosate in agriculture should enter into force in European Union by the end of 2022. More and more countries are taking restrictions on using this herbicide without waiting for the European Commission's guidance. Chemical farms will have to reorient and use more sustainable agricultural methods (growing cover crops, applying crop rotation), which will reduce weeds and improve the quality of degraded soil, which is currently deteriorating sharply in Lithuania.

Today's target message states that farming without plough equals sustainable agriculture. It is important to assess whether sustainable tillage will make it possible not to use glyphosate and whether this will increase the need for other herbicides. It is expedient to grow various cover crops in the crop rotation in order to be able to evaluate their benefits for soil properties, weeds and crop yield.

#### Hypothesis

In cultivated loamy soils, where weediness is low and dicotyledonous weeds are predominant, the introduction of catch crops into crop rotation is expected to limit herbicides, including glyphosate, in winter wheat and winter oilseed rape.

#### The aim

To evaluate the impact of various tillage and integrated technologies, including pre-crop selection, catch crops, and minimum use of herbicides, soil properties, weed infestation, soil seed bank, and productivity and economic efficiency of winter wheat and winter oilseed rape.

#### **Research tasks**

1. To determine the influence of different intensities of tillage and integrated technology on the soil physical properties.

2. To investigate the influence of tillage of various intensities and integrated technology on the change of soil chemical properties, including organic matter content.

3. To investigate the influence of tillage of various intensities and integrated technology on green hous gass emmisions.

4. To evaluate the change of weediness in winter wheat and winter oilseed rape crops by applying tillage and weed control technologies of different intensities.

5. To study the changes of weed seed bank in the soil by applying different tillage and weed management technologies.

6. To determine the influence of different tillage and weed management technologies on the yield of winter wheat and rapeseed and the quality of grain (seeds).

7. Carry out a cost-effectiveness assessment.

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# THE EFFECT OF MINERAL AND LIQUID ORGANIC FERTILIZERS ON PRODUCTIVITY OF WINTER WHEAT

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## ABSTRACT

The recycling of organic waste in manure is considered to be one of the major solutions to get rid of the wastes. It is known that manure is a natural organic fertilizer obtained directly after animal farming. Anaerobic digestate is a substrate of manure and plant wastes, left after biogas production, is also excellent for plant fertilization and soil improvement.

The aim of this study was to determine the regularities of winter wheat yield formation by fertilizing plants with mineral and liquid organic fertilizers. The field experiment was conducted in 2019 and 2020 in the northern part of Central Lithuania's lowland at the Joniskelis Experimental Station of LAMMC. A winter wheat cultivar 'Patras' was grown. Mineral fertilizer: ammonium nitrate and 2 organic fertilizers: pig slurry and liquid anaerobic digestate obtained under biological decomposition of pig slurry and residues of agriculture crops were used as separate fertilizers after the resumption of winter wheat spring vegetation; rates of fertilizers were calculated by nitrogen (N120). The effects of each type of fertilizer were studied with and without additional fertilization. For this purpose, ammonium nitrate (+N50) at the flag leaf stage was used.

During the experimental years, it has been noticed that the effectiveness of fertilizers depended on the meteorological conditions during crop formation and had an influence on winter wheat grain yield productivity indicators. The year differed significantly, in the favorable year 2020 the average winter wheat grain yield was 19% higher compared to the dry in the first half of 2019 vegetation. In the dry year (2019), mineral nitrogen fertilizers (N120) were more efficient, compared to liquid organic fertilisers. Additional fertilisation (+N50) equalized the differences in grain yield. In 2020, pig slurry increased the grain yield of winter wheat in favor of 3.7-4.3 percent. pcs., liquid anaerobic digestate 6.1-6.2 percent. pcs., as compared to ammonium nitrate. In a dry season, the winter wheat yield was increased by ammonium nitrate, whereas in a year of sufficient humidity, by liquid organic fertilizers.

Keywords: ammonium nitrate, pig slurry, liquid digestate, yield components

#### **INTRODUCTION**

One of the most important intensification factors of crop production is plant nutrition and fertilization [2]. Inputs of nitrogen to agricultural production systems are necessary to produce food, feed and fiber and to minimize negative environmental effects [3] especially when climate change and increasingly frequent extreme weather events are further expected to intensify in Europe. In recent years, considerable growth in sustainable production has been observed and organic fertilizers have been used in large quantities throughout Europe. Using organic fertilizers, farming systems should be less reliant on resource imports, at the same time supporting and soil productivity [11]. Renewable energy plays an important role in the reduction of greenhouse gas emissions. Biogas produced in agricultural biogas plants, where the substrates are animal wastes (manure), the biomass of plants specially cultivated for this purpose, and waste from the agricultural and food industry and distilleries. Biogas residue - anaerobic digestate is a relatively new type of waste and its production increased with a crescent need to be sustainable disposal. Digestate contains a high amount of organic carbon, total N content and other nutrients, which are most used as a soil amendment or bio-fertilizer for planted field crops and pastures [5]. Livestock slurry and biogas digestate have recently been used in large quantities throughout Europe as valuable fertilizers [4]. It is maintained that digestate can be an effective way to reduce nitrogen losses compared with mineral fertilizers when using the same N rates [19]; however, the yield may not always differ significantly [9, 13], and the positive effect of total N incorporated with organic fertilizers may be felt after several years [1].

Despite numerous scientific findings on a positive role of digestate as soil amendment, research evaluating anaerobic digestate effects on grain production is missing. In the present study, we had compared the effect of biogas digestate, pig slurry and mineral fertilizer on the quality of productivity of winter wheat (*Triticum aestivum* L.).

## MATERIALS AND METHODS

## Field experiment and growing conditions

The field experiment was conducted in 2018-2020 in the northern part of Central Lithuania's lowland (56°12′ N, 24°20′ E) at the Joniskelis Experimental Station of the LAMMC. A winter wheat cultivar 'Patras' was used. In the first year, wheat was sown after field beans. The research was carried out on a drained clay loam *Endocalcari Endohypogleyic Cambisol* (Cmg-n-w-can). The topsoil (0–30 cm) pH is close to neutral (6.8), moderate in humus (28.1 g kg<sup>-1</sup>) and total nitrogen (Ntot 1.83 g kg<sup>-1</sup>); medium in available phosphorus (P<sub>2</sub>O<sub>5</sub> 1.41 g kg<sup>-1</sup>) and high in available potassium (K<sub>2</sub>O 3.87 g kg<sup>-1</sup>).

Pre-sowing, every year complex mineral fertilizes  $(N_{32}P_{32}K_{32})$  were applied in the whole experimental field. Mineral fertilizer: ammonium nitrate and 2 organic fertilizers - pig slurry and liquid anaerobic digestate - were used as separate fertilises after resumption of winter wheat spring vegetation. Ammonium nitrate fertilizer (N 344 g kg<sup>-1</sup>) provides half of the N in the nitrate and half in the ammonium form. Both organic fertilizers are alkaline and based on ammonium; and in the experiment were supplemented with nitrification inhibitor 3,4dimethylpyrazole phosphate (DMPP) base product Vizura ® (BASF, Germany) using 2 L ha<sup>-1</sup> rate. A detailed nutrient composition of the applied bio-fertilizers is presented in the Table 1. Each fertilizer rate per ha was calculated according to total nitrogen (N<sub>120</sub>). Fertilization was performed on March 25, 2019 at BBCH 23–25, and on April 9, 2020 at BBCH 30–31, respectively. The treatments were laid out in a randomized design with 3 replications; each replicate plot area was 75 m<sup>2</sup>. The experiment included control and 6 fertilization treatments – in half of them used additional winter wheat fertilisation  $(+N_{50})$  with ammonium nitrate at flag leaf (BBCH 37–39) stage. The second year, experiment with wheat was repeated in the same place using the same fertilization design.

		DM	Corg	N	tot	- NINILI.	N NO.	Р	K
Fertiliser	pН	g kg <sup>-1</sup>	g kg <sup>-1</sup>	g kg <sup>-1</sup>	g L <sup>-1</sup>	$g L^{-1}$	$g L^{-1}$	g kg <sup>-1</sup>	g kg <sup>-1</sup>
2019									
PS	7.5	14.3	4.53	2.32	2.37	1.90	0.01	0.23	1.44
LD	8.2	8.0	1.82	1.81	2.13	1.58	0.01	0.07	1.14
2020									
PS	7.6	31.6	10.4	2.36	2.39	1.67	0.02	0.25	1.66
LD	7.7	27.5	7.4	2.76	2.80	1.69	0.02	0.04	1.69

Table 1. Characteristic of liquid bio-fertilizes

Liquid bio-fertilisers were a pig slurry (PS) and anaerobic digestate (LD), obtained under the controlled biological decomposition from pig slurry and residues of agriculture crops.organic fertilizers are alkaline and based on ammonium; and in the experiment were supplemented with nitrification inhibitor 3,4-dimethylpyrazole phosphate (DMPP) base product Vizura ® (BASF, Germany) using 2 L ha-1 rate.

## **Meteorological conditions**

The weather data were obtained from the meteorological station, located 0.5 km away from the experimental site (Fig 1). The weather in autumn of 2018 was slightly cooler and drier as compared to the standard climate norms. Conditions for seed germination and planttillering were favorable. There were no significant deviations in temperature and precipitation during the winter season. April was an exceptionally dry month (with more abundant rainfall only at the end of May). During the summer season of 2018, the amount of precipitation was unevenly distributed as June was drier and July was over-irrigated. The lack of humidity was exacerbated by a warm month of June when the average daily temperature was 5.6°C warmer as compared to the standard climate norm (SCN).

In September 2019, an excess rainfall resulted in the difficulty to sow winter wheat. However, a slightly drier and warmer October resulted in good germination and tillering of winter wheat. The winter season was warm with little rainfall and an absence of frost. In spring, the amount of precipitation has been close to the SCN, except in April. As compared to SCN, the month of May stood out as being cooler, while June and July were warm and rainy; excess precipitation amounted to 44.2 and 40.9 mm and was unevenly distributed.





Fig. 1. Meteorogical conditions during the vegetative period of winter wheat, 2018–2019 (a) and 2019–2020 (b) at Joniškelis Experimental Station of the Lithuanian Research Centre for Agriculture and Forestry (SCN - standard climate norm)

## Parameters of plant productivity

At the hard dough stage (BBCH 87) of winter wheat, before crops were harvested, 25 plants per plot were collected to determine the number of spikes per unit area (spikes m<sup>-2</sup>), number of grains per spike and mass (g) and number of grain per unit area (grains m<sup>-2</sup>). Winter wheat grains were harvested, when the majority of plants had reached the BBCH 87 stage. The grain yield (kg ha<sup>-1</sup>) of wheat was converted to standard moisture (14%). Grain samples (1 kg) were taken from each plot for the determination of thousand grain weight (TGW). The yield index was calculated as the ratio of grain yield abovegruong mass.

### Statistical analysis

The research data are reported as average values of replications. The data were statistically processed using the analysis of variance method (ANOVA) with the SELEKCIJA software package (Raudonius, 2017). Means ( $\pm$  standard error) were separated by honest significant difference using Dunkan's method, when the F test indicated significant factorial effects at the level of P<0.05.

## **RESULTS AND DISCUSSION**

The effect of nitrogen on the development of winter wheat depends on the use of fertilizers, their rates, and the time of fertilization. During the tillering stage (BBCH 23–28) of winter wheat with sufficient nitrogen nutrition, more shoots, productive wheat spikes, nomber of grains per spike are formed; after flowering, the grain weight increases which: results in the improvement of its quality [7, 6].

The research has shown that regarding yield index, the number of productive grain spikes, the number of grains per spike, the weight of the grain per spike as well as the grain yield, were significantly influenced over the year. The weight of the grain ear and the grain yield were essentially dependent on the applied fertilizers and fertilization rates (Table 2).

	Productive	Number	Grain	Grain	
Factor	spikesper	of grais	weight	yield	Grain yield
	plant ar in $m^{-}$	per spike	per spike	index	
	Z				
Year (A)	<0.000**	<0.000**	<0.000**	<0.000**	<0.000**
Fertilisation (B)	0.211ns	0.057ns	0.002**	0.053ns	0.001**
Interaction AxB	0.537ns	0.221ns	0.380ns	0.703ns	0.097ns

 Table 2. Analysis of variance for productivity indicators of winter wheat grown under different fertilization and year condition

\*\*—differences significant at 99% probability levels, n.s.—no significant.

Due to dry season months between April of 2019 (18.8 mm) a limited number of productive wheat spikes was formed (Table 3). Used fertilizers tended to only increase the number of productive spikes. The number of grains per spike as well as the weight per grain was sufficient; the values were from 38.5 to 49.7 and 2.02 and 2.21, respectively. The number of grains per spike and grain weight tended to increase with mineral nitrogen fertilizers and higher fertilizer rates ( $N_{120 + 50}$ ). The effect of liquid organic fertilizers was less notable. The yield index, which shows the relationship between grain yield and biomass, changed significantly. The yield index as compared to the unfertilized field, increased between 1.9-5.8% due to the use of ammonium nitrate additional fertilization ( $AN_{120 + 50}$ ,  $PS_{120 + 50}$ ,  $LD_{120 + 50}$ ). The study has revealed that the year 2019 was less favorable for plants when grain yield supplement 157.6–695.4 kg ha<sup>-1</sup> or 3.2–14.0%. was obtained from the applied fertilizers. The highest grain yield supplement was obtained by using ammonium nitrate, regardless of the fertilizer rate (no significant differences were noted).

Treat ment	Number of spikes m <sup>-2</sup>	Number of grains per	nber of Grain Grain Grain Grain Grain Grain Grain Grain Grain Grain Grain Grain Grain Grain Grain Grain Grain Gr		Grain yield		
		spike	spike g	index	kg ha <sup>-1</sup>	Pct. %	
Contr ol (N <sub>0</sub> )	334ab	38,6ab	2,02ab	0,518a	4970ab	100	
AN <sub>120</sub>	373b	39,5ab	2,10ab	0,545cd	5665b	114	
PS <sub>120</sub>	345ab	38,5ab	2,04ab	0,525ab	5127ab	103	
LD <sub>120</sub>	333ab	38,8ab	2,08ab	0,533abc d	5417ab	109	
AN <sub>120</sub> +50	367ab	40,7b	2,21b	0,547d	5617ab	113	
PS <sub>120+</sub> 50	365ab	39,9ab	2,18ab	0,543bcd	5535ab	111	
LD <sub>120</sub>	341ab	39,0ab	2,13ab	0,538bcd	5468ab	110	

Table 3. The variation of yield components of winter wheat using basic and additional fertilisation in 2019

Fertilizers: AN – ammonium nitrate, PS – pig slurry, LD – liquid digestate; rates calculated by N – nitrogen

The results of correlation analysis conducted in 2019 have shown a moderate correlation between the yield of winter wheat grain and the number of productive spikes (r=0.56 \*\*). As the number of productive spikes increased from 305 to 425 m<sup>2</sup>, accordingly, the grain yield both consistently and statically increased from 4013 to 6152 kg ha<sup>-1</sup>. Productive tilleringresulted in 31.6% grain harvest (Fig. 2).



Fig. 2. Relationship between productive spikes and grain yield of winter wheat grown in 2019

In 2020, the number of productive spikes was favorable for plant growth, and in terms of productive spikes was approximately 53.7% higher as compared to 2019 (Table 4). Pig slurry and liquid digestate with additional fertilization ( $N_{120+50}$ ) increased the number of productive spikes by 25.9 and 37.2% as compared to the unfertilized field. It can be stated that the number of productive winter wheat spikes was determined not only by the applied fertilizers and their properties but also by the lower reduction of spikes during the process of vegetation. As the number of productive spikes increased, fewer grains with a decrease in their grain weight were formed. Having drawn the comparison with the data collected in 2019, the number of grains per ear decreased on average by 31.1%, whereas the grain weight decreased on average by 31.3%. Regardless of nitrogen rate, the number of grains significantly increased as a result of the total used fertilization reaching from 14.5 to 26.1% (excluding LD<sub>120</sub>) as compared to unfertilized winter wheat. The grain weight per spike changed analogously to the number of grains.

Winter wheat that was fertilized with mineral and liquid organic fertilizers accounted for 12.8-24.8% heavier ears of wheat as compared to unfertilized winter wheat. Different rates of nitrogen fertilization increased the weight of the grains inconsistently. This was due to excess precipitation during the end of June and July and also because additionally ( $N_{50}$ ) fertilized winter wheat had laid. The yield index was 18.5% lower than in the year 2019. In 2020, the grain yield was 19.0% more favorable for the growth of winter wheat as compared to data collected in 2019.

The most significant impact on winter wheat yield had the main fertilization ( $N_{120}$ ) with mineral and liquid organic fertilizers. The fertilization of winter wheat with ammonium nitrate obtained yielding supplement adequate to 1642 kg/ha<sup>-1</sup>, pig slurry - 1867 kg/ha<sup>-1</sup>, liquid digestate - 1897 kg/ha<sup>-1</sup>, or respectively 34.4, 39.1 and 39.7% more as compared to unfertilized wheat. This shows that liquid organic fertilizers ranging from 3.5 to 4.0% were more effective than ammonium nitrate. Additional fertilization with ammonium nitrate ( $N_{50}$ ) increased grain yield insignificantly between 3.3-3.9% as compared to wheat fertilized with different fertilizers ( $N_{120}$ ). Moreover, the similarity in obtained yield was noted between the fertilization of winter wheat with ammonium nitrate ( $N_{120+50}$ ) and the fertilization with liquid organic fertilizer ( $N_{120}$ ). Comparing the efficiency of pig slurry and liquid digestate ( $N_{120+50}$ ), it was found that a similar yield supplement of 2125 and 2152 kg ha<sup>-1</sup> was obtained as compared to unfertilized wither.

Treatment	Number of	Number of	Grain weight per	Grain index	Grain yield	
Troumont	spikes m <sup>-2</sup>	spike	spike g	of yield	kg ha <sup>-1</sup>	Proc. %
Control (N <sub>0</sub> )	463a	23.4a	1.25a	0.394a	4776 a	100
AN <sub>120</sub>	542abc	28.6cd	1.52bc	0.432abc	6418 bc	134
PS <sub>120</sub>	554abc	27.0bcd	1.44bc	0.441 abc	6644 bc	139
LD <sub>120</sub>	500abc	25.6ab	1.41b	0.433abc	6673 bc	140
AN <sub>120+50</sub>	538abc	26.8bcd	1.47bc	0.467c	6632 bc	139

Table 4. The variation of yield components of winter wheat using basic and additional fertilisation in 2020

PS <sub>120+50</sub>	583bc	28.5bcd	1.50bc	0.440abc	6901 bc	144
LD <sub>120+50</sub>	598c	29.5d	1.56c	0.452abc	6928 c	145

Fertilizers: AN – ammonium nitrate, PS – pig slurry, LD – liquid digestate; rates calculated by N – nitrogen

A strong correlation with the number of productive spikes (r=0.71 \*\*) was noted in 2020 grain yield and the medium strength of grain weight per spike (r=0.65 \*\*) was found. With the increase in the number of productive grains per spike from 1.22 to 1.63 g, the grain yield consistently and statically increased from 4556 to 7386 kg ha<sup>-1</sup>. Both the number of productive spikes and the grain weight per spike had a similar effect on yield with similar determination coefficients - 49.9% and 42.3%. (Fig .3 and 4).



Fig. 3. Relationship between productive spikes and grain yield of winter wheat grown in 2020





The first stage of winter wheat productivity formation is determined by the productive density, flowering, and grain fertilization, defined by the number of grains per square meter. In the second stage of winter wheat, the weight of grain is formed depending on the plant assimilation apparatus size and activity, the ability of the plant to transport assimilators to grains, grain formation time, meteorological conditions [7, 12].

The present study shows that in 2019 the productivity of winter wheat was determined by the values of the number of grains ranging from low to medium (12855\_14890 units per m<sup>2</sup>) and the high weight of 1000 grains (50–55 g.) (Fig. 5). The low number of grains per unit area was due to the low productive density although it was partially compensated by the higher number of grains per spike. Such formation of yield productivity elements was determined by the arid period (between April and May) during which the activities of the intensive tillering and groundmass growth were taking place. The greatest effect on the formation of primary indicators had the ammonium nitrate. The number of grains per square meter varied from 12855 to 14800, which shows the average values of the indicators. The highest number of grains was found after fertilization with ammonium nitrate (N<sub>120</sub>), increasing the number of grains by 10.2%. (N<sub>120+ 50</sub>) 15.8% as compared to unfertilized winter wheat. High weight of 1000 grains was determined. According to the statistical analysis, the number of grains per square meter was significantly influenced by fertilization (p <0.02) with mineral nitrogen fertilizers.



Fig.5. The effect of fertilisation on formation of winter wheat number of grains per meter and thousand grain weight in 2019



Fig.6. The effect of fertilization on formation of winter wheat number of grains per meter and thousand grain weight in 2020

## CONCLUSIONS

Meteorological conditions and nitrogen fertilization influenced winter wheat yields. In both years, a strong correlative relationship was identified between the number of productive spikes and grain yield. In a dry season (2019), the winter wheat yield was increased by ammonium nitrate, whereas in a year of sufficient humidity (2020), by liquid organic fertilizers. Yield supplement after the fertilization with liquid organic fertilizers (N<sub>120</sub>) was 157.5–447.3 kg ha<sup>-1</sup> in dry, and 1867.3–1897.0 kg ha<sup>-1</sup> in years of optimal humidity.

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# EFFECTS OF ETHYLENE AGENT ETHEPHON ON SEXUAL EXPRESSION AND CANNABINOID SYNTHESIS IN HEMP (CANNABIS SATIVA L.) PLANTS OF MONOECIOUS, DIOECIOUS AND DIFFERENT CHEMOTYPE VARIETIES IN FIELD TRIAL

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#### EXTENDED ABSTRACT

#### **OVERVIEW**

Gender of cannabis (*Cannabis sativa* L.) plants or quantitative ratio of female to male inflorescences in hermaphrodite (monoecious) varieties of hemp has a crucial role for quality of medicinal or essential oil material Male cannabis plants or male inflorescence in monoecious hemp varieties are non-productive for bioactive compounds such as cannabinoids and terpenoids and also have a significant negative impact on the yield of these secondary metabolites such as cannabinoids and terpenoid compounds in female plants or female inflorescences.

In this study, we assessed the impact of ethylene releasing agent ethephon, periodically applied by foliar spraying during the flowering period on sex expression, concentrations of main secondary metabolites, and productivity *in natura*.

Ethephon solutions of various concentrations ranging from 220  $\mu$ M/m<sup>2</sup> to 866  $\mu$ M/m<sup>2</sup> were applied on monoecious, dioecious sex type, cannabidiolic and cannabigerolic varieties of hemp: "Felina 32" (monecious, cannabidiolic), "Santhica 27" (moecious, cannabigerolic), "Kompolti" (dioecious, cannabidiolic). Effects on the hermaphroditism, on concentrations of main secondary metabolites in inflorescence, on yields of different parts of plants were assessed in two year field trial.

The study revealed that all doses of the ethephon ranging from 220  $\mu$ M to 866  $\mu$ M greatly affected plant sexual expression and turned hermaphrodite plants of monoecious hemp varieties into almost 100 % female except rare non-hermaphroditic male phenotypes. Sexual expression in dioecious hemp variety was not affected.

Some treatments with the ethephon increased cannabinoid (cannabidiol and cannabigerol) concentration in inflorescence of monoecious and dioecious hemp varieties. The highest doses of ethephon decreased the concentration of the cannabigerol in monecious cannabigerolic chemotype hemp variety.

All ethephon treatments reduced plant height and biomass yield.

#### **METHODS**

The field experiment was carried out in the fields of The Lithuanian Research Centre for Agriculture and Forestry in the middle of Lithuania, Northern Europe.

Three different varieties of hemp were sown on 15<sup>th</sup> of May 2019 and 2020.

- "Felina 32": monoecious, cannabidiol dominant, moderate early variety.
- "Santhica" 27: monoecious, cannabigerol dominant, moderate early variety.
- "Kompolti": dioecious, cannabidiol dominant, late flowering variety.

Plants were treated with a foliar spray every two weeks since inflorescence started to form (middle of July) until full maturity.

Treatments were:

- Control (water)
- $220 \,\mu M/m^2$
- $440 \,\mu M/m^2$
- $660 \,\mu M/m^2$
- 880 μM/m<sup>2</sup>

Every treatment had 4 repetitions.

Seven phenotypes regarding the ratio of female to male inflorescence were determined.

0-100 % male flower phenotype (very morphologically distinct, thin, and tall plants)

1-80-99 % of male inflorescence (morphologically similar to female plants but taller, almost all inflorescence is male).

2-60-80 % of male inflorescence (morphologically similar to female plants)

3 - 40-60 % of male inflorescence

4 – 60-80 % of female inflorescence

5 - 80 - 95 % percent of female inflorescence

6-100 % of female inflorescence

As hemp plants fully revealed their sex, 50 plants from each repetition of every treatment and every hemp variety were evaluated.

The quantity of every phenotype in percent was determined.

Cannabinoids CBD and CBG were determined by using gas chromatography system Shimadzu GC 2010 Plus with spectrometric mass detector QP 2010 using reference standards from "Lipomed AG". According to "Recommended Methods For The Identification And Analysis Of Cannabis Products" by UN Office on drugs and crime ST/NAR/40.

Data was subjected to the statistical analysis using SAS Enterprise data analysis software.

One-way analysis of variance (ANOVA) followed by uncan multiple range tests were employed, and differences between individual means were deemed to be significant at p<0.05. The values are  $\pm$ SD for four samples in each group.

#### RESULTS

All concentrations of ethephon ranging from 220 µM to 8 µM significantly

decreased hermaphroditism in monoecious hemp varieties "Santhica 27" and "Felina 32" during both growing seasons 2019 and 2020. All treatments diminished hermaphroditic phenotypes from 1 to 5 (means are given in above in section "Methods") and increased the quantity of 100 % female phenotypes.

All treatments significantly decreased the quantity of "80-99% female" sex phenotypes in "Santhica 27", "Felina 32", very few of these phenotypes were left.

Sex phenotypes: "60-80 female", "40-60% female", "60-80 % male", and "80-99 % male" were not apparent in all ethephon treatments.

Only quantity of non-hermaphroditic, 100 % male phenotype was not affected in "Santhica 27" and "Felina 32" varieties during both growing seasons.

The sex of monoecious variety "Kompolti" was not affected - no male hermaphrodite plants were detected.

All most all ethephon treatments increased concentrations of main cannabinoids in inflorescence of hemp at full maturity in monoecious and dioecious cannabidiolic chemotype and monoecious cannabigerolic chemotype hemp varieties.

#### CONCLUSIONS

Foliar application of ethephon solutions of doses ranging from 220 to 880  $\mu$ M/m2 significantly reduced the quantity of hermaphrodite phenotypes in monoecious and dioecious hemp fields except 100 percent male phenotype in seasons 2019 and 2020.

Foliar application of ethephon solutions of doses ranging from 220 to 880  $\mu$ M/significantly increased concentration of main cannainoids CBD and CBG respectively in plants of cannabidiolic and cannabigerollic chemotype monoecious varieties in seasons 2019 and 2020.

Treatmens of 220  $\mu$ M/m2, 660  $\mu$ M/m2 and 880  $\mu$ M/m2 increased CBD concentration in plants of cannabidiolic dioecious variety "Kompolti" in seasons 2019 and 2020.

Doses of ethephon ranging from 220 to 880  $\mu$ M/m2 did not affect sexual expression in male or female plants of dioecious hemp variety "Kompolti" in seasons 2019 and 2020.

Keywords: (Times New Roman, 10 pt, text justified, Line spacing 1.0, space before: 12 pt)

# CHARACTERISATION OF SOIL MICROBIOTA DECOMPOSING THE PLANT RESIDUES IN CEREAL BASED CROPPING SYSTEM: A REVIEW

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#### EXTENDED ABSTRACT

#### **OVERVIEW**

In sustainable agriculture the conservation and restoration of soil fertility are some of the most important challenges. Organic enrichment as a source of humus is one of the means of maintaining soil fertility. The amount of organic matter in the soil depends directly on the balance between its synthesis and degradation. In farming systems, this depends on the crops and organic waste they leave behind. As a rule, plant waste is released into the soil, where it begins to decompose. Knowledge of the mineralization of crop residues introduced into the soil is fundamental to soil management objectives aimed at maintaining and restoring soil organic matter (SOM) and for predicting long-term SOM trajectories [1]. As a result, harvesting in agriculture and forestry generates a large amount of plant residues. The global production of biomass residues is about 140 Gt. [2,3]. The burning of crop residues produces air pollutants and greenhouse gases, as well as particles and hydrocarbons that affect the chemical composition of the atmosphere [4]. In addition, incineration or disposal of residues can lead to a decrease in microbial biomass and activity compared to soils where plant residues are returned to the soil [5]. Decomposition products of crop residues, such as nitrogen (N), cellulose, lignin, and polyphenols, play a role in the rate of release of nutrients from residues and hence in the subsequent rate of uptake of nutrients by cash crops. The straw of most cereal crops contains about 35, 10 and 80% of the total N, P and K respectively taken up by the crop [6]. In this review, we focus on studies aimed at using cellulolytic microorganisms as plant residue decomposers.

World production of winter wheat straw in 2013 was 529 million tons [7] with a world production of 710 million tons of grain [8]. Estimated global wheat production in 2020 is around 765 million tons [9]. Thus, at present the production of straw can reach 569 million tons. Global information on the application of straw to the soil is not available and crop residues are still needed to maintain soil organic matter. The fertility and therefore the quality of the soil depends on the turnover of organic carbon in soils and, that is on the introduction of organic matter in the soil. The rate at which soil organic C is decomposed responsible for the turnover of organic C pools [10] and thus soil health. One of the key indicators of soil degradation is the loss of soil organic carbon (SOC) from agricultural soils due to the loss of net primary productivity in crop production systems worldwide [11]. The importance of crop residues is very high in maintaining soil quality because plant residues are the most important source of soil organic matter in agricultural systems [12].

Cellulose is the most abundant biological compound in terrestrial and aquatic ecosystems and is the main component of plant biomass [13]. It is a common waste from the agricultural industry in the form of stems and husks. It is worth noting the great interest in the use of cellulose as an energy resource and feed [14]. Cellulose is tasteless, odorless hydrophilic with a contact angle of 200-300, insoluble in water, and most organic solvents are chiral and biodegradable. It can be chemically decomposed into glucose units by treatment with concentrated acids at higher temperatures [15]. Cellulose is formed from D-glucose units that condense through  $\beta$  (1  $\rightarrow$  4) - glycosidic bonds. It is a vital structural part of the primary cell wall of green plants, many forms of algae, and the most abundant organic compound on Earth [16], available worldwide.

Many types of microorganisms affect the decomposition of plant residues. It has been established that fungi are the main microorganisms degrading cellulose, but several types of bacteria and actinomycetes have been reported [17], which also produce cellulase and are involved in the degradation process [18]. Cellulolytic and hemicellulolytic bacteria have been isolated from a wide variety of environments, such as soil, compost, decaying plant waste, and ruminant feces [19]. Bacteria and actinomycetes play an important role in the biodegradation of plant debris during composting [20, 21].

Currently, along with other enzymes, fungal cellulases are used in several industries. The most important fungal genera reported with a large amount of cellulase production for industrial use belong to *Trichoderma, Colletotrichum, Penicillium, Aspergillus, and Fusarium* [22]. Amongst all species of *Trichoderma, T. reesei* is very well documented for its diverse type of cellulases used in different industries [23]. Besides these, isolates of *Aspergillus* and *Penicillium* are also high cellulase producers used in the hydrolysis of biomass and biofuel production [24].

A large number of Gram-positive and Gram-negative species of bacteria are reported to produce cellulase including *Clostridium thermocellum, Streptomyces spp., Ruminococcus spp., Pseudomonas spp., Cellulomonas spp., Bacillus spp., Serratia, Proteus, Staphylococcus spp.,* and *Bacillus subtilis* [25,26]. These bacteria can degrade cellulose derived from different agricultural or forest wastes and convert it into value-added products [27].

#### CONCLUSIONS

The decomposition of wheat straw is essentially a microbiological process that significantly affects the formation and functioning of soils. Currently, there are methods such as composting or direct incorporation of crop residues into the soil to solve the problem of maintaining organic matter in the soil, unfortunately they are laborious and time-consuming. Therefore, the use of cellulose-degrading microorganisms as plant residue decomposers might be a suitable method for accelerating decomposition rate, reducing environmental pollution due to crop residue burning and the use of chemical fertilizers, as well as for creating a path for sustainable agriculture.

Keywords: crop residue decomposition, cellulose, cellulose degrading microorganisms

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# THE INFLUENCE OF ORGANIC FERTILIZERS ON ABUNDANCE OF SOIL MICROORGANISMS COMMUNITIES, AGROCHEMICAL INDICATORS AND YIELD IN EAST LITHUANIAN LIGHT SOILS

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#### EXTENDED ABSTRACT

#### **OVERVIEW**

Soil microorganisms are one of the main indicators for assessing the stability of the soil ecosystem, the metabolism in the soil and its fertility. By supporting biogeochemical cycles, they accelerate the decomposition of plant residues, producing nitrogen compounds available to plants. In terms of the listed processes, the most important are the active soil microorganisms and the influence of the fertilizer applied to the soil on the abundance of these microorganisms.

This article describes a study to determine the quantitative changes of soil microorganism communities in infertile soils of east Lithuania. The aim is to investigate how the applied organic fertilizers affect the most active soil microorganisms, which determine the soil fertility and stability, mineral nitrogen concentration in soil and spring barley yield. The study was launched in 2018 in fourteen experimental fertilization variants. Fungal, yeast-like fungal abundance and abundance of three physiological groups of bacteria were analysed: non-symbiotic diazotrophic, organotrophic, and mineral nitrogen assimilating.

#### **METHODS**

Quantitative research of soil microorganisms is performed in the Lithuanian Research Centre for Agriculture and Forestry in the laboratory of the Vokė branch. The two most used types of organic fertilizers for agricultural crops selected from the investigation were poultry and cattle manure (litter and granulated). These fertilizers differ in the amount of nutrients (concentration) and the intensity of nutrient release. Non-commercial biological additive has been used in the experiment: nitrogen-fixing bacteria *Azotobacter vinelandii* (No 1) - A; biological substance containing the fungus *Trichoderma* spp. (No 2) - T. The quantitative analysis is performed using the dilution method by inoculating the soil suspension on appropriate agar media. The analyses of soil agrochemical properties are performed before and after the test installation the investigation. The barley grain yield is determined from the cuttings. The straw yield is calculated according to the determined ratio.

#### RESULTS

The results of 2020 quantitative analysis of culturable soil microorganisms showed, that the highest abundance of organotrophic  $(119\pm21\times10^3 \text{ CFU/g} \text{ of dry soil})$  and non-symbiotic diazotrophic  $(147\pm38\times10^3 \text{ CFU/g} \text{ of dry soil})$  bacteria were recorded during the summer season. Meanwhile, the abundance of bacteria assimilating mineral nitrogen  $(180\pm40\times10^3 \text{ CFU/g} \text{ of dry soil})$  and fungi  $(2.87\pm1.24\times10^3 \text{ CFU/g} \text{ of dry soil})$  were higher in autumn. The results of dispersion analysis of the performed study shows, that fertilization had the greatest effect on the spread of bacteria during the summer season, and in autumn for fungi. Agrochemical parameters were determined at the beginning of the experiment. The highest concentration of N<sub>min</sub> in the soil was determined by fertilizing the plants with the combination of granulated granulated poultry manure  $(N_{170})$  + biological substance No 1. The yield of barley was calculated. It was found that the highest yield of spring barley in 2020 was obtained by fertilizing the experimental field with organic in combination with mineral fertilizers.

#### CONCLUSIONS

The investigation results of the quantitative analysis of soil microorganisms in 2020 demonstrated that the abundance of organotrophic and non-symbiotic diazotrophic bacteria was the highest during the summer period. The highest abundance and population peaks of mineral nitrogen-assimilating bacteria and fungi were registered in the autumn.

The investigations of mineral nitrogen in the soil in a stationary field experiment have demonstrated that the concentration of mineral nitrogen depends not only on fertilization with organic fertilizers, but also on meteorological conditions in the winter-spring period.

The highest grain and straw yield were recorded in cases when the soil was fertilized with one mineral fertilizer and while adding mineral fertilizer rates to the granulated poultry manure.

Keywords: physiological groups of soil microorganisms, fertilization, agroecosystems

# GRASS BIOMASS AND CARBON DYNAMICS IN DIGESTATE – TREATED SOIL

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#### ABSTRACT

The aim of the present study was to estimate the distribution of soil organic carbon within the 0–30 cm layer and the increase in grass biomass as influenced by digestate fertilisation. The experiment was carried out in Surviliskis ( $55^{\circ}26'03.07''$  N  $24^{\circ}02'12.26''$  E), Kedainiai district (Central part of Middle Lithuanian Lowland), on a semi-natural perennial grassland in 2018 and 2019. The grassland had been in use for 10 years before the experiment. The experiment included five fertilisation treatments: without fertilisation; fertilisation with separated liquid digestate at 85 and 170 kg ha<sup>-1</sup> N, fertilisation with separated solid digestate at 85 and 170 kg ha<sup>-1</sup> N, the size of each plot was 6 m<sup>2</sup>. A randomised experimental design with three field replicates was used. Fertilisation was performed and samples of soil and grass biomass were taken for two consecutive years. The highest accumulation of soil organic carbon in the digestate-treated soil was determined in the 0-10 cm soil layer. The increase in grass biomass (1.2–2.5-fold) was found in all fertilisation treatments compared to the control (without fertiliser). The highest annual dry matter yield of grasses was determined in the plots fertilised with separated liquid digestate at 170 kg ha<sup>-1</sup> N (2018 – 5.85 t ha<sup>-1</sup>, 2019 – 4.98 t ha<sup>-1</sup>). The results of the study showed that digestate applied as a biofertiliser was important not only for the increase of grass biomass but also as a potential soil improver promoting accumulation of soil organic carbon.

Keywords: digestate, soil organic carbon, grass yield

#### INTRODUCTION

Anaerobic digestion is a prevalent processing method of agricultural wastes, which minimises the negative environmental impact. The biological decomposition of organic matter is performed in an oxygen-free environment. During this process, biogas and a waste product - digestate are obtained. Biogas can be used as renewable energy. The digestate is rich in macroand micronutrients and can be applied to the soil to improve its quality or as a biofertiliser [1].

The waste product of biogas production can be applied to the soil without processing or after mechanical separation into solid digestate and liquid digestate. The digestate is a reservoir of organic carbon and plant nutrients but it indicates quantitative and qualitative differences: the solid digestate contains 38–75% of highly stable organic matter and a low NH<sub>4</sub>-N/total-N ratio; the liquid digestate has a low organic matter concentration and a high NH<sub>4</sub>-N/total-N ratio. The use of solid digestate as a soil amendment can aid soil carbon sequestration, especially in intensively cultivated soils where plant residues are removed from the field. The liquid digestate is more suitable for use as the biofertiliser [2].

Soil organic carbon (SOC) is the carbon of soil organic matter. It is important for the effect on soil fertility, plant growth and productivity. SOC plays an important role in soil and water conservation. Also, SOC increases the nutrient cycling capability of soil [3]. Unsuitable grazing and mowing are harmful to plants and soil carbon stocks. When grassland ecosystem is sequestering atmospheric CO<sub>2</sub>, carbon stocks can be rebuilt [4]. The most important driver for SOC changes in the soil is the carbon input via root and above-ground litter, and additional organic amendments, which is determined by the balance of carbon inputs over losses [5,6].

The spreading of digestate as a fertiliser for grasslands could be one of the ways to utilize residues from biogas production [7]. Grasslands are important ecosystems worldwide. They sequester carbon in plant biomass and soil organic matter as well as produce most of the forage for ruminants [8].

The aim of the present study was to estimate the distribution of soil organic carbon within the 0-30 cm soil layer and the increase in grass biomass as influenced by fertilisation with different rates of solid and liquid digestate.

## MATERIALS AND METHODS

The experiment was carried out in Surviliskis (55°26′03.07″ N 24°02′12.26″ E), Kedainiai district (Central part of Middle Lithuanian Lowland), in perennial grassland on a glacial morain *Endocalcaric Albic Brunic Endogleyic Arenosol (Dystric)* according to WRB [9]. The botanical composition of the grassland was dominated by plants of the Poaceae family. The experiment was established in 2018 and continued for 2 consecutive years (2018 and 2019). Five fertilisation treatments were investigated: without fertilisation, fertilisation with separated liquid digestate at 85 and 170 kg ha<sup>-1</sup> N and with separated solid digestate at 85 and 170 kg ha<sup>-1</sup> N, based on the results of the chemical analysis of the digestate. A randomised experimental design with three field replicates was used. The plot size was 6 m<sup>2</sup>. Dry and liquid digestate was spread on the grassland manually. The experiment was set up on the permanent seminatural grassland, which had been used for forage production for 10 years.

Fertilisation was performed and samples of soil and grass biomass were taken for two consecutive years. Soil samples were taken with a steel auger from three replications of the topsoil (0–10, 10–20 and 20–30 depth) in October. The dry matter yield (DMY) of grassland was determined by weighing. Herbage was cut manually twice depending on the grass growth stage.

To determine the dry matter, grass samples of approximately 0.5 kg were collected from each plot and dried at a temperature of +105 °C. Soil organic carbon content was determined by Tyurin method modified by Nikitin [10,11].

Statistical analysis. The data were analysed using the software SAS Enterprice, version 7.1 (SAS Institute Inc., USA). The analysis of variance (ANOVA) was performed to determine the effects of digestate fertilisation on SOC content and annual grass dry matter yield. The data were compared using Fisher's least significant difference (LSD) test at the probability level of P < 0.05.

## **RESULTS AND DISCUSSION**

There are many factors and processes that determine the rate of change in SOC. One of them is increasing the input rates of organic matter, that is important for magnification of SOC storage [13]. The present study estimated the distribution of SOC within the 0–30 cm layer as influenced by fertilisation with different rates of liquid and solid digestate.

**Table 1.** Soil organic carbon (SOC) content as influenced by fertilisation with solid and liquid digestate in 2018 and 2019 (\* – significantly different at P < 0.05).

Treatment	Soil layer	SOC g	g kg <sup>-1</sup>
	cm	2018	2019
Control	0-10	11.8	11.7
(no fertiliser)	10-20	8.39	8.72
	20-30	3.99	4.00
	Mean 0-30	8.05	8.14
Solid digestate	0-10	12.8	12.5
85 kg ha <sup>-1</sup> N	10-20	9.34	9.39
	20-30	4.54	5.15
	Mean 0-30	8.89	9.01
Liquid digestate	0-10	13.1	13.8*
85 kg ha <sup>-1</sup> N	10-20	8.71	9.12
	20-30	4.70	5.20
	Mean 0-30	8.82	9.37
Solid digestate	0-10	13.5	13.4
170 kg ha <sup>-1</sup> N	10-20	8.85	8.71
	20-30	4.21	5.53
	Mean 0-30	8.85	9.21
Liquid digestate	0-10	13.4	14.1*
170 kg ha <sup>-1</sup> N	10-20	9.78	9.84
	20-30	4.29	4.86
	Mean 0-30	9.14	9.75
$LSD_{05}$	0-10	2.58	1.86
	10-20	2.89	3.73
	20-30	2.74	2.63
	Mean 0-30	3.76	3.66

Soil organic carbon content increased in all digestate-treated plots in 2018. The highest SOC amounts (12.8–13.5 g kg<sup>-1</sup>) were determined in the 0–10 cm layer (Table 1). This represented 1.0–1.6 g kg<sup>-1</sup> increase over the control treatment (without fertilisation). The same trend was observed in 2019: the highest SOC amounts (12.5–14.1 g kg<sup>-1</sup>) were determined in the 0-10 cm layer, the increase over the control treatment was 0.8–2.4 g kg<sup>-1</sup>. A statistically significant difference between the treatments (0–10 cm) was observed when the grassland was

fertilised with liquid digestate rates of 85 kg ha<sup>-1</sup> N and 170 kg ha<sup>-1</sup> N in 2019. Soil organic carbon increased with increasing organic matter accumulation in the soil. For this reason, digestate can be a source of organic matter in the soil, as well as an important tool for stabilization and sequestration of SOC [13, 15].



**Figure 1.** The dry matter yield of grasses t ha<sup>-1</sup> (2018)

(1st - first cut; 2nd - second cut; control - without fertilisation; 85 N solid - solid digestate 85 kg ha<sup>-1</sup> N; 85 N liquid - liquid digestate 85 kg ha<sup>-1</sup> N; 170 N solid - solid digestate170 kg ha<sup>-1</sup> N; 170 N liquid - liquid digestate170 kg ha<sup>-1</sup> N). *Note. Error bars are shown as standard error* 





(1st - first cut; 2nd - second cut; control - without fertilisation; 85 N solid - solid digestate 85 kg ha<sup>-1</sup> N; 85 N liquid - liquid digestate 85 kg ha<sup>-1</sup> N; 170 N solid - solid digestate170 kg ha<sup>-1</sup> N; 170 N liquid - liquid digestate170 kg ha<sup>-1</sup> N). *Note. Error bars are shown as standard error* 

The highest soil organic carbon content was determined in the plots fertilised with a liquid digestate rate of 170 kg ha<sup>-1</sup> N. The accumulation of organic carbon in the soil depended on the digestate rate, which agrees with the results of similar studies on digestate use as a soil amendment and fertiliser [2, 14, 15]. The accumulation of organic carbon may also have

contributed to the SOC increase in the deeper soil layers. The results confirm that digestate can be applied to improve soil C sequestration and to compensate for carbon depletion associated with biomass removal [2]

The dry matter yield of grasses varied depending on the rate of the biofertiliser and the year (Figs. 1 and 2). DMY in all fertilised treatments were statistically significantly (P>0.05) higher compared with the control. In the first year of the study, the total DMY of herbage ranged from 3.12 to 5.85 t ha<sup>-1</sup>, in the second year it ranged from 1.88 to 4,98 t ha<sup>-1</sup>.

The plots fertilised with liquid digestate at a rate of 170 kg ha<sup>-1</sup> N produced the highest DMY yield. A slightly lower but also good increase in DMY was observed in the plots fertilised with 85 kg ha<sup>-1</sup> N of liquid digestate (4.77 t ha<sup>-1</sup>) and 170 kg ha<sup>-1</sup> N of solid digestate (4.76 t ha<sup>-1</sup>) in 2018. Different results in these plots were obtained in 2019: the yield increase amounted to 4.13 t ha<sup>-1</sup> and 2.67 t ha<sup>-1</sup> respectively. In general, the DMY of the second cut was lower than of the first cut. The lower total DMY yields in 2019 may have been caused by a long period of drought in the spring and in June (according to http://www.meteo.lt/lt/desimtadieniu-agrometeorologiniu-salygu-archyvas), especially in the plots fertilised with 170 kg ha<sup>-1</sup> N of solid digestate.

This study indicates the need to continue field experiments in order to verify and validate the obtained results and to more comprehensively assess the most important agronomic effects of digestate application. However, based on the findings from the 2-year experiment, it can be concluded that the use of digestate as biofertiliser allows production of large amounts of biomass and can reduce the use of mineral fertilisers. It is also a way to manage the digestate produced during biogas production [16].

## CONCLUSIONS

- For all treatments, the highest accumulation of soil organic carbon was found in the 0-10 cm layer of *Arenosol*. The highest soil organic carbon content in the 0-30 cm layer was determined in the plots fertilised with a separated liquid digestate rate of 170 kg ha<sup>-1</sup> N.
- 2. An increase in the grass biomass (1.2–2.5-fold) was determined in all fertilisation treatments compared to the control (without fertiliser). The highest annual dry matter yield of grasses was produced in the plots fertilised with 170 kg ha<sup>-1</sup> N of separated liquid digestate 5.85 t ha<sup>-1</sup> in 2018 and 4.98 t ha<sup>-1</sup> in 2019.
- 3. The results of the study showed that digestate as a biofertiliser was important not only for the increase of grass biomass but also as a potential soil improver promoting accumulation of soil organic carbon, which stimulates carbon sequestration in the soil.

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## THE USE OF HEMP BIOMASS FOR SOIL QUALITY IMPROVEMENT

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#### ABSTRACT

Climate change and soil degradation aretwo of the most important environmental problems today that need urgent solutions. To avoid catastrophic effects on global society, every effort should be made to keep the average temperature increase below 1.5 ° C. Therefore, in addition to the rapid reduction of greenhouse gas emissions, it is necessary to look for alternative ways of storing carbon and minerals in the soil [1]. It is expected that carbon stocks in the soil may be increased by effective management of agricultural biomass. One of the potential sources of biomass is hemp (Cannabis sativa L). Hemp is grown worldwide and is one of the oldest sources of food, textile fibre and medicine. As a result, the present study will aim to evaluate the potential of hemp biomass used as a soil additive for the amendment of soil quality and plant growth. In the twentieth century, due to the competition from increasingly lucrative raw materials such as cotton and synthetic fibres, hemp production has gradually declined, with the exception of France, where hemp pulp and paper production (mainly supplied by French producers) has allowed some land stability [2]. In addition to the traditional use of hemp fibre, its use as a reinforcement in biocomposites (mainly in car industry), insulation materials and other nonwovens (technical textiles) has increased in recent years [3]. Nowadays hemp is mainly used for the extraction of cannabidiol (CBD) or other bioactive compounds. Flowers and a small part of biomass are used for the CBD extraction; therefore, it is expected that the rest of the biomass could be used for soil improvement. Nevertheless, there is very limited information about the degradation of hemp biomass in the soil and its effect on soil carbon accumulation.

Keywords: hemp, soil, biomass.

### **INTRODUCTION**

Climate change and soil degradation are two of the most important environmental issues these days. To avoid catastrophic effects on global societies, every effort must be made not to increase the average temperature by more than 2°C [4]. Therefore, there is the need for rapid reductions in greenhouse gas emissions and alternative ways of storing carbon and minerals in the soil. But it is not just climate change that threatens the balance of planetary ecosystems [5], for example, soil degradation has resulted, among other things, from unsustainable methodological and subsequent deforestation by farmers seeking new artificial lands, which also poses a direct threat to global biodiversity [6]. One of the ways to increase soil organic carbon might be the use of natural organic compounds for soil improvement or effectively utilize the residual biomass in agricultural management systems. The aim of this paper is to analyse the potential of high yielding hemp growth and use for production of different products as well to identify the research level on the use of hemp biomass for soil quality improvement. One of the highest problems of growing hemp is huge content of residues and straws.

## **Brief Methodology**

Data and literature were collected from Web of Science eBooks Freedom Collection (ScienceDirect) <u>https://www.sciencedirect.com/;</u> Statistical information collected from Hemp indrusty Daily and The State plant service under the ministry of agriculture of Lithuania.

## **Results and discussion**

Growing of hemp in EU. Hemp (Cannabis sativa L.) is grown worldwide and is one of the oldest sources of medicine, food and textile fiber. Aspects and agronomic methods of hemp cultivation in Central and Southern Europe have always been designed with textile and clothing in mind. In the twentieth century due to competition from increasingly lucrative raw materials such as cotton and synthetic fibers, hemp production is gradually declining, with the exception of France, where hemp pulp and paper production (heavily supplied by French producers) has allowed the stability of their land [2]. In 2018 it was about 50,081 hectares of hemp in Europe (Fig. 1). Even as weather conditions in southern Europe are suitable for hemp growth there is little background knowledge regarding the productivity of the recently registered varieties due to the interruption of hemp production in the second half of the last century. However, many farmers are interested in the reintroduction of hemp cultivation more than 50 % of all hemp fields in Europe are in France, Italy and Netherlands [9]. Almost the same amount of occupied hectares - 56,196 was in 2019 [7]. The main problems faced by the renewal of industrial hemp cultivation in Europe include the selection of the most appropriate variety to European conditions, the lack information regarding the agronomic data to incorporate into farming systems and practices, the end use of the final product, and the negative attitude towards hemp cultivation due to the THC content [10].



Fig. 1 Cannabis fields statistics in Europe [8]

Farmers have been allowed to grow hemp only since 2014 in Lithuania, the declared area under this crop was over 1000 hectares in the same year [9]. After 5 years hemp crop occupied around 9000 hectares.

**Hemp productivity.** The observed difference in hemp biomass yield  $(3.4-31.2 \text{ tha}^{-1})$  was due to environmental conditions, applied fertilization, plant density, and genotypes [10–12]. The highest biomass yield is set in Italy. Northern Italy – 28,6-31,2 t/ha dry matter [13], central Italy – 13,1-26,3 t/ha dry matter [11], Latvia – 13,5-21,3 t/ha dry matter [10], the least yield in Southwest Germany – 5,2 -12,8 t/ha dry matter [12]. The most popular hemp cultivar of biomass is "Felina 32", "USO 31", "Epsilon 68", "Finola" [14].

**The use of hemp.** Hemp fiber is one of the greenest and oldest of all natural fibers. In addition to the traditional use of fibers, in recent years their use as reinforcement in biocomposites (various cars), insulation materials and other nonwovens (technical textiles) has increased in response to the growing need for biologically clear sustainable and recyclable materials [11,15]. However one of the highest problems of hemp growing is huge content of residues of straw and leaves, which could be used to help to improve soil quality.

Hemp is widely used, with a grain content of usually 25-35% oil, 20-25% protein, 20-30% carbohydrates and 10-15% insoluble fiber as well as a rich set of minerals [3,11,16] "In addition", "hemp seed oil" positive health benefits, including lowering cholesterol and blood pressure [17]. Currently, highly polyunsaturated hemp seed oil as personal care products such as lotions, moisturizers, shampoos and lip balms [16].

Hemp seeds are versatile and developed for many products in food, cosmetics, therapeutic, functional food and nutrition industries [11,16]. The production of hemp seeds and the fixed properties of the oil vary greatly, depending on the variety depending on the date of harvest and the agro-climatic and geographical conditions in which they grow [11].

The influence of hemp on soil quality. Hemp loosens and softens the soil, and the fallen foliage forms mulch that preserves the material and bacteria in the soil [18]. After harvesting, the root system decays rapidly. If hemp is in the field, up to two-thirds of the organic matter returns to the soil [19]. Hemp plants reduce the population of nematodes and pathogenic fungi in the soil and can be grown without the use of pesticides, herbicides or fungicides [20,21]. It is argued that the introduction of hemp in crop rotation can improve soil health [18]. On the other hand there is limited information about hemp fiber degradation in the soil and its influence on soil quality and crop productivity therefor new research is needed.

## CONCLUSIONS

More and more hemp is grown in Lithuania and Europe. Hemp is not only widely used for the production of different products, but also can contribute to greenhouse gas reduction. Hemp nowadays is mainly used to extract CBD and other active compounds, to make healthy food supplements, cosmetics products or for natural fibers. However, one of the highest problems of growing hemp is huge content of residues of leaves or straws. One of sustainable ways to use hemp residues could be production of organic fertilizers or pellets for heating from hemp biomass.

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# **DEEP SOIL PLOUGHING FOR AFFORESTATION**

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## **EXTENDED ABSTRACT**

Deep ploughing is ploughing to a depth of 30–45 cm or deeper, depending on soil type [1-4]. In Europe, deep ploughing dates to the 1950s, and this technology was mainly used in agriculture. Site preparation for forest regeneration has been practiced since humans began managing forests, and it is a recurring theme in forest policy groups [5, 6]. Deep ploughing is rarely used due to environmental concerns. However, it should be considered as an alternative technology when planning afforestation of former agricultural land [1, 7-9]. This paper summarises the empirical evidence on the ecological effects of deep soil ploughing and suggests specific indicators for deep ploughing responses in afforested sites, contributing to risk assessments for sustainable forest management.

This theoretical study highlights key aspects of deep soil ploughing, which is a practice where the soil is usually cultivated deeper than 30–45 cm, typically with the aim of reducing soil compaction, and encouraging deeper plant rooting and growth through improved soil aeration, water infiltration, and nutrient availability. Selecting the appropriate ploughing method can eliminate limiting factors such as high-density subsoil, intensive accumulation of organic litter, vigorous weed cover, allelopathic vegetation, or soil compaction induced by harvesting machines.

Although deep ploughing can be used under different climatic and soil conditions, the responses of soil and vegetation to deep ploughing were found to be site specific. Finding a compromise between the advantages and disadvantages, deep soil ploughing destroys soil functionality, and the changes associated with it continue for at least 30 years. Most studies on mechanical site preparation and forest plantation performance have been conducted using a few conifer tree species; therefore, it is appropriate to conduct more local experimental studies.

Keywords: deep tillage, afforestation, soil mixing, soil properties, vegetation response

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# GROWTH PROPERTIES OF PEA PLANTS IN RESPONSE TO THE COMPLEX EFFECTS OF DIFFERENT NANOPARTICLES AND DROUGHT STRESS

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#### ABSTRACT

This study aimed to explore the effects of molybdenum (Mo; 35-45 nm), boron (B; 100 nm), copper oxide (CuO; 25-55 nm), and silicon dioxide (SiO<sub>2</sub>; 20-30 nm) nanoparticles (NPs) at three concentration levels (0.05 mg ml<sup>-1</sup>; 0.025 mg ml<sup>-1</sup>; 0.0125 mg ml<sup>-1</sup>) and drought stress on pea plant growth parameters including shoot and root length, fresh biomass, and leaf area as well as the number of root nodule. The experiments were carried out in greenhouses during the spring-summer period. 10-liter pots with 5 plants in each (n=35) were arranged in a completely randomized manner. Pea plants were exposed to drought for 10 days after they were watered or sprayed with different NPs suspensions. CuO NPs showed a statistically significant positive effect on pea shoot height, root length, and the number of nodules when the concentration of sprayed NPs suspension was 0.0125 mg ml<sup>-1</sup>. Mo NPs had the strongest positive effect on the measured plant's properties when peas were irrigated with 0.05 mg ml<sup>-1</sup> NPs suspension. B NPs were most effective when plants were sprayed at the concentration of 0.05 mg ml<sup>-1</sup> under drought conditions. SiO<sub>2</sub> NPs were most effective when plants were watered or sprayed with 0.05 mg ml<sup>-1</sup> NPs suspension.

Keywords: Molybdenum NPs, Silicon dioxide NPs, Boron NPs, Copper oxide NPs, Pisum sativum, biomass, shoot, root.

## **INTRODUCTION**

Important interests in the use of nanotechnologies in agriculture include specific applications such as nanofertilizers and nanopesticides, to quantify products and nutrients, to increase productivity without contaminating the soil, water, and protecting against several insects pests, microbial diseases, and stress. Nanotechnologies can act as sensors to monitor the quality of agricultural soil in the field and thus maintain the health of crops [1].

Copper (Cu) is widespread in plant tissues and is an essential trace element for growth and is involved in many physiological processes. There are several reports of toxicity of CuO NPs to plant morphology, germination and product quality, transpiration, and plant tissues [2]. However, no experiments with peas have yet been performed.

Molybdenum (Mo) is an important element in the plant nitrogen fixation system. In this context, it has been reported that the treatment of nitrogen-fixing bacteria in chickpea seeds with Mo NPs increased them two or three times compared to water treated. It was concluded that Mo NPs can improve plant nutrition and increase bacterial activity [3]. However, it remains to be determined which Mo NPs concentration is most appropriate for pea plants.

Boron (B) is an essential trace element in the development of nitrogen-fixing root nodules in peas. B deficiency causes many biochemical, physiological, and anatomical changes in plants

[4]. The effects of nano-sized B on peas have not yet been studied, and it must also be determined whether it can act on bacteria in nodules formed on pea roots.

The effects of silicon (SiO<sub>2</sub>) on plant growth, yield, and resistance to biotic and abiotic impacts can be very pronounced. SiO<sub>2</sub> acts as a physical-mechanical barrier and is placed on the epidermal walls and stem vascular tissues, the leaf coat of most plants [5]. It also controls the physiological activity of plants. SiO<sub>2</sub> NPs provide better seed germination, ensuring easier access to nutrients in seeds. Also, SiO<sub>2</sub> NPs can improve seedling growth and quality, including mean height, root length and diameter, and the number of seedling lateral roots.

This experiment aimed to investigate the complex effects of different concentrations of copper oxide, molybdenum, boron, and silicon nanoparticles and drought stress on pea plant shoot and root length, fresh biomass, leaf area, and the number of root nodule.

## METHODOLOGY

#### Nanoparticle suspension

Nanoparticles (NPs) suspension was prepared with deionized water at concentrations of 0.0125, 0.025, and 0.05 mg ml<sup>-1</sup>. Copper oxide (CuO), molybdenum (Mo), boron (B), and silicon (SiO<sub>2</sub>) NPs were purchased at the respective sizes of 25-55nm, 35-45 nm, 100nm, and 20-30nm (US Research Nanomaterials, Inc, Houston, TX USA). The suspension was dispersed by using an ultrasonicator for 60 min. The suspension stability and NPs size were measured using Zeta Potential device (Dispersion Technology Inc., Bedford Hills, New York) and Delsa<sup>TM</sup>Nano Submicron Particle Sizer (Beckman Coulter Instruments. Corporation, Fullerton, California).

#### **Plants and growth conditions**

The experiment was carried out in the greenhouses of LAMMC Institute of Horticulture during the spring-summer period of 2019. Seeds of peas ("Respect" Maribo Seed International ApS, Denmark) were sterilized in 5% NaClO solution for 30 min, then were gently washed and soaked in water for 24h. 10 peas were sown in the loam in each 10 L vegetative container. Plants were affected by NPs when they reached the 40-59 stage on the BBCH scale. Randomly selected vegetative pots with pea plants were divided into four parts: part of the plants were watered or sprayed with NPs suspension and grown under normal conditions (optimal substrate moisture (40-50%)); another part of the plants was watered or sprayed with NPs suspension and then exposed to drought for 10 days. Drought was caused by maintaining lower substrate moisture (4-8%). Weather conditions during the experiment are presented in Table 1. The shoot height, root length, number of root nodules, and fresh weight of 10 randomly selected plants were measured for each treatment.

2019	Temperature, C <sup>o</sup>		Humi	dity, %
	Day	Night	Day	Night
Before drought	24.2	14.4	54.1	75.3
During drought	26.2	17.0	50.1	73.2
After drought	26.7	16.6	52.8	73.5

Table 1. The average temperature and humidity during the experiment.

## **Statistical Analysis**

Results were analyzed using analysis of variance (ANOVA) followed by Tukey HSD at  $p \le 0.05$  to determine significant differences. Statistical analyses were performed using XLSTAT (Xlstat, Addinsoft, Paris, France, 2020).

## RESULTS

More than 50% of the particles of the prepared suspensions were found to be up to 100 nm and it was observed that cumulation of Mo and  $SiO_2$  NPs was lower than CuO and B.



Fig. 1. CuO (a), Mo (b), SiO<sub>2</sub> (c), and B (d) NPs size distribution in suspensions at a concentration of 0.05 mg ml<sup>-1</sup>.

The greatest positive effect of CuO suspension on pea shoot height (5%), fresh biomass (13%), and leaf area (13%) was found for plants sprayed with 0.0125 mg ml<sup>-1</sup> under normal conditions. The most increase in pea root length (24%) was observed when plants were watered with 0.05 mg ml<sup>-1</sup> CuO suspension (Table 2). The greatest effect on pea shoots height (9%), root length (46%), leaf area (14%), and the number of roots nodules (88%) were observed for plants sprayed with the lowest concentration of NPs suspension in drought conditions (Table 2).

Table 2. Effect of CuO NPs suspension on pea shoot height, root length, fresh weight, and the number of root nodules, compared to control (W0). W – watered, S – sprayed. A stronger statistically positive effect is indicated by red; the opposite effect is indicated by blue. Statistical reliability Tukey (HSD): \*p <0.05; \*\*p<0.01; \*\*\*p<0.001)

	Concentration (mg ml <sup>-1</sup> ) of NPs suspension	Shoot height (cm)	Root length (cm)	Number of root nodule	Fresh biomass (g)	Leaf area (cm <sup>2</sup> )
	W 0.05	25.83	13.9*	3.8	2.60	29.932**
	W 0.025	26.95	12.6	3.0	2.52	30.244*
During normal	W 0.0125	27.15	10.5	0.5	2.70	31.166
conditions	S 0.05	27.00	12.2	4.5 *	2.59	32.437
	S 0.025	28.73*	8.7	1.8	3.46***	33.113*
	S 0.0125	28.25*	12.0	2.0	3.47***	38.444***
Control	W 0	27.18	10.5	1.8	3.02	34.083
	W 0.05	23.40	11.8	3.0	2.13	27.160**
	W 0.025	26.35	10.1	2.3	2.48	28.982**
During drought	W 0.0125	27.33*	9.2	0.8	2.87*	32.608
conditions	S 0.05	21.78	11.7	4.5	2.39	31.620
	S 0.025	27.2*	12.4	1.8	2.53	30.017*
	S 0.0125	28.4**	18.9**	8.0 **	2.65	37.893***
Control	W 0	25.98	10.2	1.0	2.71	33.136

Table 3 shows that irrigation with 0.05 mg ml<sup>-1</sup> Mo NPs suspension under normal conditions had the greatest effect on pea shoot height (22%), root length (47%), number of root nodules (85%), fresh biomass (56%) and leaf area (24%). Similar results were found in drought conditions; shoot height increased by 24%, root length by 35%, number of nodules by 85%, fresh biomass by 52%, and leaf area by 37% when plants were watered with 0.05 mg ml<sup>-1</sup> Mo NPs suspension. In general, a stronger statistically significant effect on pea was observed when plants were watered with Mo NPs suspension.

Table 3. Effect of Mo NPs suspension on pea shoot height, root length, number of root nodules, and fresh weight compared to control (W0). W – watered, S – sprayed. A stronger statistically positive effect is indicated by red; the opposite effect is indicated by blue. (Statistical reliability Tukey (HSD): \*p<0.05; \*\*p<0.01; \*\*\*p<0.001)

	Concentration (mg ml <sup>-1</sup> ) of NPs suspension	Shoot height (cm)	Root length (cm)	Number of root nodule	Fresh biomass (g)	Leaf area (cm <sup>2</sup> )
	W 0.05	36.3***	19.8**	11.3***	6.92***	44.852***
	W 0.025	35.7***	17.2**	11.0***	4.46**	40.863**
During normal	W 0.0125	30.3	11.6	2.0	4.21*	35.345
conditions	S 0.05	33.4***	15.6*	3.3	6.09***	43.069**
	S 0.025	29.7	13.7	1.8	3.98	36.107
	S 0.0125	30.5	13.2	1.8	3.80	33.010
Control	W 0	28.4	10.5	1.8	3.02	36.083
	W 0.05	34.4***	15.7*	6.8***	5.68***	41.373**

During drought conditions	W 0.025	30.5***	13.9*	4.5*	3.58	31.285
	W 0.0125	28.4	12.5	1.5	3.46	30.323
	S 0.05	32.2***	13.8*	5.3**	4.12*	38.927**
	S 0.025	28.6	11.6	4.3*	3.31	36.926*
	S 0.0125	27.0	12.0	1.3	3.13	36.393*
Control	W 0	26.0	10.2	1.0	2.71	30.136

The statistically significant effects of B NPs were observed after growing peas under normal conditions. It was observed that watering of pea plants with the highest concentration of B NPs suspension increased their shoot height (21%), fresh biomass (29%), and leaf area (31%), but decreased root length (40%) (Table 4). Also, all growth indices increased after spraying pea plants with the lowest B NPs concentration. Considering the highest concentration of B NPs sprayed on peas and drought conditions, a significant increase in root length (30%) and increased number of nodules (93%) were observed.

Table 4. Effect of B NPs suspension on pea shoot height, root length, number of root nodules, and fresh weight compared to control (W0). W – watered, S – sprayed. A stronger statistically positive effect is indicated by red; the opposite effect is indicated by blue. (Statistical reliability Tukey (HSD): \*p<0.05; \*\*p<0.01; \*\*\*p<0.001)

	Concentration (mg ml <sup>-1</sup> ) of NPs suspension	Shoot height (cm)	Root length (cm)	Number of root nodule	Fresh biomass (g)	Leaf area (cm <sup>2</sup> )
	W 0.05	36.1***	7.5***	9.5***	4.24***	47.147***
	W 0.025	30.7	12.1	5.0***	3.87***	40.205*
During normal	W 0.0125	32.2***	8.7*	10.3***	3.46*	45.022**
conditions	S 0.05	33.2***	12.1	5.3***	3.84***	46.129**
	S 0.025	31.3**	10.8	5.5***	3.85***	45.693**
	S 0.0125	36.2***	12.7	7.0***	4.64***	49.829***
Control	W 0	28.4	10.5	1.8	3.02	31.109
	W 0.05	30.6***	12.3	8.5***	3.84***	43.763*
	W 0.025	32.8***	12.4*	6.0***	3.55***	43.374*
During drought	W 0.0125	28.6*	12.4*	2.3	2.77	28.404***
conditions	S 0.05	29.5***	14.5*	13.8***	3.51***	47.147**
	S 0.025	31.8***	13.0*	3.0*	3.15*	33.626*
	S 0.0125	29.2**	11.0	1.8	2.83	31.396*
Control	W 0	26.0	10.2	1.0	2.71	36.083

A statistically positive effect of the irrigated 0.05 mg ml<sup>-1</sup> SiO<sub>2</sub> NPs suspension was observed on pea plants when they grew under normal conditions. It was observed, that shoot height, the number of nodules, fresh biomass, and leaf area of pea plants increased by 24%, 81%, 33%, and 31% respectively. Moreover, sprayed 0.05 SiO<sub>2</sub> NPs concentration on pea plants had a positive effect on shoot height (18%), root length (54%), number of nodules (56%), fresh biomass (25%), and leaf area (24%) in drought conditions (Table 5).

Table 5. Effect of  $SiO_2$  NPs suspension on pea shoot height, root length, number of root nodules, and fresh weight compared to control (W0). W – watered, S – sprayed. A stronger

	Concentration (mg ml <sup>-1</sup> ) of NPs suspension	Shoot height (cm)	Root length (cm)	Number of root nodule	Fresh biomass (g)	Leaf area (cm <sup>2</sup> )
	W 0.05	37.3***	12.0	9.3***	4.50***	47.332**
	W 0.025	36.6**	12.0	6.8***	3.71*	42.309**
During normal	W 0.0125	30.0	12.1*	4.5*	3.35	38.164*
conditions	S 0.05	28.9	11.7	3.8	3.43	38.854*
	S 0.025	29.4	11.3	4.3*	3.26	36.434
	S 0.0125	29.5	11.0	2.8	3.01	36.373
Control	W 0	28.4	10.5	1.8	3.02	36.083
	W 0.05	35.5***	10.9	2.5	3.68*	41.044***
	W 0.025	31.7***	11.7	2.0	3.61*	39.914**
During drought	W 0.0125	33.6***	10.4	2.0	3.35	37.498*
conditions	S 0.05	31.7***	12.4*	2.3	3.62*	40.050**
	S 0.025	28.9	11.9	2.5	3.25	36.763*
	S 0.0125	27.8	11.2	3.0	2.92	33.454
Control	W 0	26.0	10.2	1.0	2.71	33.136

statistically positive effect is indicated by red; the opposite effect is indicated by blue. (Statistical reliability Tukey (HSD): \*p<0.05; \*\*p<0.01; \*\*\*p<0.001)

## DISCUSSIONS

It should be emphasized that drought has many negative effects on plants, they are smaller, weaker, and can lead to a significant reduction in yields. Certain nanoparticles can help plants avoid the effects of drought.

Depending on the concentration of Cu it can be both toxic and beneficial to plants. In this study, CuO NPs were found to have a positive effect on plant height, weight, leaf area, root length, and the number of root nodules when was watered or sprayed with 0.0125 mg ml<sup>-1</sup> concentration (Table 6). While CuO NPs have a toxic effect on pea at a concentration of 0.05 mg ml<sup>-1</sup> during drought conditions. Other researchers have found that CuO has a toxic effect on soybean at a concentration of 0.5 mg ml<sup>-1</sup> [2]. This difference may be because peas have a weaker antioxidant system than soybeans and are less resistant to abiotic stress [6, 7]. These different responses of plants can be explained by the different activity of the antioxidant system and resistance to abiotic stress.

The most favorable conditions for rhizobia were observed when plants were watered with Mo NPs at 0.05 mg ml<sup>-1</sup> concentration in normal or drought conditions. In these plants, the number of nodules was up to 6 times higher compared to the control plants. Similar results were found by other scientists in the experiments with chickpeas [3]. The soaked chickpea seeds Mo NPs (0.008 mg ml<sup>-1</sup>) before sowing had a significant effect on root nodules compared to the control plants. Thus, it can be concluded that the higher the Mo NPs concentration, the more nodules are formed on the plant roots.

Moreover, exceptionally by spraying the pea plants with the highest B NPs concentration, a positive effect on root formation and the number of nodules under drought conditions were obtained. Specifically, B is required for certain plant-derived glycoproteins, which are very important as signals of bacteria differentiation into the N<sub>2</sub>-fixing form [4].

In this study,  $SiO_2$  NPs had a marked positive effect on the aboveground part of peas and no significant effect on the number of nodules in drought conditions. Similar experiments by other researchers have shown that 0.06 mg L<sup>-1</sup> SiO<sub>2</sub> NPs significantly mitigated the negative
effects of salt stress on germination percentage, root and shoot length, and lens (*Lens culinaris* Medic.) seedling weight [5]. Similar effects were observed in our research with pea plants. Table 6. Percentage effect on peas grown with drought stress after exposure to the most effective concentration of NPs.  $\blacksquare$  - decrease;  $\uparrow$ - increase.

	CuO	Мо	В	SiO <sub>2</sub>	
	$0.0125  mg  ml^{-1}$	0.05 mg ml <sup>-1</sup>	$0.05 \text{ mg ml}^{-1}$	0.05 mg ml <sup>-1</sup>	
Shoot height	0	19	12	18	
Root length	46	26	30	54	
Number of root nodules	88	81	93	56	
Fresh biomass	2	34	23	25	

# CONCLUSIONS

The studied CuO, Mo, B, SiO<sub>2</sub> NPs affected pea shoot and root length, number of root nodules, fresh biomass, and leaf area. The effect of NPs was mainly dependent on NPs concentration, growth conditions, and application of NPs on pea plants but depending on their concentration the effect can be both. For peas, the best effect was observed with 0.05 mg ml<sup>-1</sup> Mo, B, and SiO<sub>2</sub> NPs.

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# INFLUENCE OF INTERCROPPING WITH AROMATIC PLANTS ON BIOCHEMICAL COMPOSITION OF CABBAGE

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### EXTENDED ABSTRACT

#### **OVERVIEW**

Intercropping is valued for its potential to increase crops' yield, benefits for soil, and efficient land use [1-3]. Additionally, it is an environmentally friendly way to protect crops from pests [4-8] as aromatic plants produce phytoncides which provide defending properties. Vegetables are an important element of a human diet. Brassica oleracea vegetables are widely cultivated and economically valuable [9]. Cabbages are a source of vitamins, organic acids, glucosinolates, anthocyanins, amino acids, minerals, and other bioactive compounds [10,11]. The effect of different intercropping systems on cabbage nutrient contents was examined [3]. However, the influence on cultivated crop quality parameters must be known before intercropping with certain plants. It is essential to ensure the highquality production of cabbages to increase the added value of these vegetables. Many studies are linking intercropping to pest protection [4–8], some of them investigating aromatic plants [2,12,13]. Aromatic plants accumulate various metabolites with antimicrobial, antioxidant, insect repellent, herbicidal properties [14]. Intercropping with aromatic plants may lead to exposed pesticidal properties [12], and a higher yield as less production is lost. An essential aspect of this farming method is the impact on vegetable quality. The biochemical composition of cabbages was studied under different cultivation methods [15]. However, the effects of intercropping on the biochemical quality of vegetables have not been thoroughly analyzed. There is a lack of information on nutritional value changes, mineral composition, and other qualitative components of cabbages grown under intercropping conditions. Intercropped aromatic plants, processing pesticidal volatiles should have a neutral or positive impact on crops to be recommended for application in agricultural practices. Whereas this study aimed to determine the effect of intercropping with calendula (Calendula officinalis L.), tagetes (Tagetes patula L.), thyme (Thymus vulgaris L.), and sage (Salvia officinalis L.) on the biochemical composition of white cabbage.

### **METHODS**

The research took place at the Institute of Horticulture, Lithuanian Research Centre for Agriculture and Forestry in 2017-2018. The experimental design was a randomized block with three replications, size of the replicate field  $-7 \text{ m}^2$ . One row of white cabbage cultivar 'Krautman F1' followed one row of aromatic plants (calendula, tagetes, thyme, and sage) repeatedly in the experimental field. All intercrops were compared with the cabbage monoculture (control). Biochemical parameters of cabbages were determined after harvesting: dry matter (%), total sugar (%), ascorbic acid (mg/100 g), nitrogen (N, %), potassium (K, %), phosphorus (P,%), magnesium (Mg, %) and calcium (Ca, %).

#### **RESULTS AND DISCUSSION**

Due to the observed lack of qualitative studies on the composition of crops after intercropping, this study focused on the biochemical analysis of cabbages. Similar results between growing years were observed in the mineral composition of cabbages intercropped with aromatic plants. Results of nitrogen, potassium, phosphorus, magnesium, and calcium percentage varied between the treatments and were close to cabbage monoculture in both experimental years. Results are in agreement with the previous study, where no significant differences were determined in the mineral composition of cabbages intercropped with aromatic plants had lower sugars than cabbage monoculture except for cabbage-tagetes in 2017. Meanwhile, no significant differences for this parameter were observed in 2018. Results are comparable to total sugar content

determined in Chinese cabbages grown under both organic and conventional farming systems [15]. The dry matter did not vary much in treatments between experimental years. Overall, higher content of ascorbic acid was determined in 2018 than in 2017. Calendula and thyme in the intercropping system caused the highest ascorbic acid amount in cabbages in 2018.

#### CONCLUSIONS

Two years of observations revealed that intercropping with aromatic plants did not affect the biochemical composition of cabbages. To sum up, calendula (*Calendula officinalis* L.), tagetes (*Tagetes patula* L.), thyme (*Thymus vulgaris* L.), and sage (*Salvia officinalis* L.) can be grown together with white cabbage, to improve the phytosanitary conditions of vegetables without compromising biochemical quality.

Keywords: intercropping, cabbage macronutrients, sustainable horticulture, vegetable quality.

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# EFFECTS OF MINERAL FERTILIZERS ON GRASSLANDS OF DIFFERENT SPECIES COMPOSITION

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### ABSTRACT

The object of the research is different grass-legume swards and possibility to decrease the use of mineral nitrogen fertilizers, the excessive use of which in agriculture is one of the causes of environmental pollution. Excessive concentrations of nitrogen fertilizers threaten soil fertility, surface and groundwater quality. Grass-legume mixtures characterized by high productivity, efficient nitrogen (N) use and strong weed suppression were proposed to increase sustainability of grassland production. In intensively managed grasslands, even modest increases species richness can result in strong yield benefits, when species are selected for complementary traits. The grassland field experiments were conducted from 2018 at the Lithuanian Agriculture and Forestry Sciences Centre, located in Akademija, Central Lithuania. Mixtures with one, three, four, six and eight grassland species were sown in experimental areas. The experiment was equipped with two backgrounds using mineral nitrogen fertilizers N<sub>150</sub> and N<sub>0</sub>. The use of mineral nitrogen fertilizers in mixtures with legumes has been found to inhibit their growth. Fertilization has a positive effect on grass plants more than legumes. The annual two years experiment dry matter yield of the fertilized experiment was 9% higher compared to the unfertilized experiment. More diverse grassland crops increase yield resilience. Manipulate species and functional group diversity have a positive effect to yield. This experiment offers novel insights for both agronomy and ecology.

Keywords: grasses, legumes, multi-species, diversity

## **INTRODUCTION**

Ecosystem processes vary through time in response to disturbances and environmental fluctuations. Unfavorable environmental conditions both in Lithuania and in the world cause significant losses to agriculture every year due to reduced plant growth and productivity. The main negative effects on agricultural crops are caused by natural stressors: unfavorable weather conditions, outbreaks of diseases and pests. The ability of plants to adapt to the negative effects of environmental stressors can determine their growth and development, and to predict and control these processes, it is particularly important to study the mechanisms of stressors exposure and plant adaptation.

Permanent grasslands host a high plant diversity, which sustains many ecosystem services. Cultivating mixtures of different plants can be one of the sustainable means of increasing agricultural productivity, but it is very important to optimize functional diversity by combining different species characteristics that are well adapted to local growing conditions [1,13]. The mixture composition effects on total herbage in various harvests [2].

Recently more attention has been devoted to the sustainability of grasslands: nitrogen cycle, maintenance of biodiversity and soil fertility [4]. Studies shows that soil nitrogen (N), carbon (C), phosphorus (P) and Magnesium (Mg) positively correlated with plant biomass [9], suggesting that soil nutrients rather than plant diversity play critical roles in regulating plant biomass accumulation.

Species diversity is a major determinant of ecosystem stability, productivity, and nutrient dynamics [5,14]. Hundreds of studies show that high-diversity mixtures are

approximately twice as productive as monocultures of the same species and that this difference increases through time [3]. These impacts of higher diversity have multiple causes, including interspecific complementarity, greater use of limiting resources, decreased herbivory and disease, and nutrient-cycling feedbacks that increase nutrient stores and supply rates over the long term [12].

Plant diversity and biomass production relationship in grasslands, has gain great interest among ecologists in the 21st century. Nutrients are an important limiting factor for grasslands growth. Excessive use of synthetic fertilizers in grasslands causes environmental problems. Also the use of synthetic fertilizers contributes to the increase in greenhouse gas emissions. Nitrous oxide (N<sub>2</sub>O) emissions in grasslands contribute considerably to global warming and are influenced substantially by nitrogen deposition [6,11]. Therefore, it is important to include Nfixing plants in grasslands that can capture biological nitrogen from the atmosphere to reduce the need for synthetic fertilizers. Reduced N fertilizer application may mitigate N<sub>2</sub>O emissions [7].

The aim of the present study was to identify the influence of different grass-legume mixtures with different species and functional group diversity on the yield productivity of the first and second year of sward use with annual fertilizers rate in grasslands  $N_{150}$  and  $N_0$  respectively. The research object is mineral nitrogen fertilizers, the excessive use of which in agriculture is one of the causes of environmental pollution.

# METHODOLOGY

We carried out our field study in grassland plots at the Lithuanian Research Centre for Agriculture and Forestry, located in Akademija (55°383'N, 23°861'E), Central Lithuania. 2018 was the year of sowing, 2019 first and 2020 second year of sward use. All treatments were fertilized with the same rate of standard mineral fertilizer ( $5 - 20, 5 - 36 \text{ kg N} - P - \text{K ha}^{-1}$ ) in spring 2018. The main agrochemical characteristics of the top soil layer (0-25 cm) measured at the beginning of the experiment in 2018 (Table 1).

Soil depth, cm			Results		
	pH (KCl)	Phosphorus	Potassium	Soil	Nitrogen,
	suspension,	$(P_2O_5)$	(K <sub>2</sub> O)	organic	(N <sub>sum</sub> ), %
	mol/l	concentration,	concentration,	matter	
		mg/kg	mg/kg	(SOM)	
				%	
0-10	6,9	232	215	3,26	0,245
10-25	6,8	208	131	2,86	0,248
Average	6,9	220	173	3,06	0,247

Table 1. The main agrochemical soil characteristics before conducted experiment

The soil of the experimental site is a loamy Endocalcaric Epigleyic Cambisol. Neutral soil pH 6,9 and relatively high organic matter content 3,06 % with high plant available P 220 mg kg<sup>-1</sup> and K 173 mg kg<sup>-1</sup>.

Two factors were investigated: A – different grass/legume mixtures, B – two level of mineral nitrogen (N) ferilization ( $N_0$  – no N fertilization and  $N_{150}$ )).

The 12 different mixtures (A factor) were sown consisted of grasses. The dominant plant species were perennial ryegrass (*Lolium perenne* L.) cv. Elena DS (*L.p.*), meadow fescue (*Festuca pratensis* L.) cv. Raskila (*F.p.*), *xFestulolium* L. cv. Vėtra (*xF.*), timothy (*Phleum pretense* L.) cv. Dubingiai (*P.p.*) and legumes white clover (*Trifolium repens* L.) cv. Dotnuviai (*T.r.*), red clover (*Trifolium* pratense L.) cv. Sadūnai (*T.p.*), sainfoin (*Onobrychis viciifolia* L.) cv. Meduviai (*O.v.*), lucerne (*Medicago sativa* L.) cv. Malvina (*M.s.*).

In this experiment were used new, less investigated, Lithuanian varieties of four grasses and four legumes plants. Mixtures with one, three, four, six and eight grassland species was sown in experimental areas. Legume/grass ratio in the sown mixtures was 40:60 (Table 2). We established twelve plots (each 1,5 m  $\times$  10 m) with four replicates. The experiment had a randomised block design.

Treatment	Functional	Species	FG	FG	Grasses		Legumes					
	groups		Grass	Legumes	L.p.	<i>x F</i> .	<i>F.p.</i>	<i>P.p.</i>	<i>T.r</i> .	Т.р.	M.s.	<i>O.v.</i>
1	1	1	1		1							
2	1	1	1			1						
3	2	3	0.6	0.4	0.6				0.2	0.2		
4	2	3	0.6	0.4		0.6			0.2	0.2		
5	2	4	0.6	0.4	0.3	0.3			0.2	0.2		
6	2	6	0.6	0.4	0.15	0.15	0.15	0.15	0.2	0.2		
7	2	4	0.6	0.4	0.3	0.3			0.2			0.2
8	2	6	0.6	0.4	0.15	0.15	0.15	0.15	0.2			0.2
9	2	4	0.6	0.4	0.3	0.3			0.2		0.2	
10	2	6	0.6	0.4	0.15	0.15	0.15	0.15	0.2		0.2	
11	2	6	0.6	0.4	0.3	0.3			0.1	0.1	0.1	0.1
12	2	8	0.6	0.4	0.15	0.15	0.15	0.15	0.1	0.1	0.1	0.1

Table 2. Composition of mixtures with different species in sowing for swards establishing.

The grassland plots had received N fertilizer at 150 kg N ha<sup>-1</sup> year<sup>-1</sup> in three times per seazon ( $N_{60}$  in spring,  $N_{45}$  after first and  $N_{45}$  after second cut). The grass had been harvested 4 times per year in 2019 and 5 times per year in 2020. The 2020 year of grassland use was a warm and sufficiently humid year compaired with 2019.

The first yields of swards were taken before flowering stage of grasses, 8 and 6 weeks after start of vegetation in 2019 and 2020 respectively. To determine the biomass dry matter (DM), portions of 1 - 1.5 kg fresh biomass was oven dried at 105 °C to constant weight for each harvest sample by performing the sward botanical composition analysis. An analysis of variance (ANOVA) was conducted to analyse the effects of the treatment. Significant differences between the experimental treatments were determined using Duncan's test at the 0.05 probability level and Two – way analysis of variance to determine the effect of nitrogen fertilizers on grasslands of different species composition compared to unfertilized.

## **RESULTS AND DISCUSSIONS**

The results of the first year of sward showed significant effect (p < 0.05) of species richness on yield productivity. Sward yields of eight-species communities (treatment 12) were 48 % higher than monocultures average of perennial ryegrass and xFestulolium. The average of grasslands diversity with six plant species (treatment 8) were 52 % higher, the difference between six and eight plant species mixtures were 7 % (676 kg ha <sup>-1</sup>). In the evaluation of legumes, lucerne and red clover had the most possitive effect on DM yield of swards. Less productive in the mixtures were white clover and sainfoin. Higher yields was found in the interaction of xfestulolium with red clover accordingly 10 % more than with perennial ryegrass. Xfestulolium has better growth properties and in the remaining grass mixtures. Non-nitrogen fertilized perennial ryegrass and xfestulolium grasses developed more slowly according the yield was lower and no significant differences were found between these monocultures separately. There was a tendency that lucerne was the most productive species and the highest amounts of dry matter were recorded in mixtures with this legume. The average biomass yield of the remaining mixtures was 26 % lower. Dry matter yields were significantly increased by

diversity of multi-species, but not all species individually had a significant effect on sward productivity.

Analyzing both factors - fertilization and diversity of mixture composition the results showed mineral fertilizers had significant impact in the annual dry matter yield for the four treatments - monocultures (treatments 1, 2) and grasslands of four and six plant species (treatments 9, 10), which did not contain lucerne and red clover hence white clover and sainfoin do not have a significant effect on the overall increase in sward productivity during the first year of sward use (Fig. 1).

The highest annual dry matter yield using mineral nitrogen fertilizers was found in a mixture of 4 plant species (treatment 7), without mineral fertilizers in a mixture of 6 plant species (treatment 8). In addition, the yield is higher at 1399 kg ha<sup>-1</sup> in a mixture of more diverse species composition without the use of additional mineral fertilizers. Mineral fertilizers used in treatments 9 and 10 with legumes - sainfoin and white clover increased yields. The lucerne was less supressed by the use of nitrogen as a red clover or other legume species.



Fig. 1. Annual dry matter (DM) yield in the 1st year of sward use: the interactions of nitrogen fertilizers and manipulation diversity of mixtures. Grasses: G1 - perennial ryegrass, G2 - X festulolium, G3 - meadow fescue, G4 – timothy; Legumes: L1 - white clover, L2 - Red clover, L3 – lucerne, L4 – sainfoin. N0 and N150 – level of nitrogen fertilizer per year.

Annual yield showed that there was an insignificant differences (p > 0.05) between monocultures and swards with higher species richness by using 150 kg N fertilization. With the use of mineral fertilizers N<sub>150</sub>, the annual yield of perennial ryegrass monocultures increases 1,5 times, accordingly xfestulolium 1,7 times compaired with N<sub>0</sub> rate. Indeed this is equivalent to the yield that can be obtained by adding at least two legumes suitable for growing together in a mixture with these grasses. Mineral nitrogen fertilizers contributed to the growth of grasses in mixtures, but reduced the growth potential of legumes (Table 3).

Table 3. 1st year 2019 of sward use average difference between individual species in mixtures

Grasses/Legumes										
	Perennial	X	Meadow	,	White	Red				
	ryegrass	festulolium	fescue	Timothy	clover	clover	Lucerne	e Sainfoin	Forbs	
$\mathbf{N}_0$	1347	3162	872	359	194	2372	3838	270	114	
$N_{150}$	2231	4868	899	928	20	657	1295	211	277	
		Increased				Ree	duced			
Difference,	,									
kg ha <sup>-1</sup>	+884	+1706	+27	+569	-174	-1715	-2543	-59	+164	

The grassland ecosystems are affected by natural and anthropogenic factors. Therefore, their productivity is not constant and research shows that it changes due to many factors, the biggest influence of which is the dominance of the most important perennial grass species, meteorological conditions, fertilization and use [8, 10]. Different studies reported that the mixtures composition effected on biomass productivity of swards and each component differently [2,15], however diversity of mixtures have positive influence [11].

In the second year of sward use (Table 4), compared to the first, a marked increase yield of legumes without nitrogen use White clover with 77 % higher yield, red clover 42 % and lucerne 19 %. The yield of the sainfoin remained constant as timothy grass. Fertilization had the significant impact on the meadow fescue grow, yield increased by 38 %.

Table 4. 2nd year 2020 of sward use average difference between individual species in mixtures

Grasses/Legumes									
	Perennial	Х	Meadow		White	Red			
	ryegrass	festulolium	fescue	Timothy	clover	clover	Lucerne	Sainfoin	Forbs
$\mathbf{N}_0$	1608	2039	905	402	834	4105	4758	270	79
N <sub>150</sub>	3402	4088	1457	987	42	1422	2260	257	175
	1	Increased				Ree	duced		
Difference,									
kg ha <sup>-1</sup>	+1794	+2049	+552	+586	-792	-2683	-2497	-12	+96

An analysis of two factors found that mineral nitrogen fertilizers significantly increased only the yield of monocultures. In the second year of grassland growth, the total highest dry matter yield was found in the interaction of white and red clover with xfestulolium without the use of mineral nitrogen fertilizers, the yield was 10 177 kg ha <sup>-1</sup>, 9459 kg ha <sup>-1</sup> yield obtained using mineral nitrogen fertilizers in monoculture.



Fig. 2. Annual dry matter (DM) yield in the 2nd year of sward use: the interactions of nitrogen fertilizers and manipulation diversity of mixtures. Grasses: G1 - perennial ryegrass,
G2 - X festulolium, G3 - meadow fescue, G4 - timothy; Legumes: L1 - white clover, L2 - red clover, L3 - lucerne, L4 - sainfoin. N0 and N150 - level of nitrogen fertilizer per year.

The use of nutrient resources is a very important factor in terms of competition and compatibility of species, and their quality of existence and productive growth in the same place at the same time. To meet the nutrient demand in the agroecosystem, biological nitrogen-fixing legumes were used in the mixtures, the effect of which was compared with the effect of mineral fertilizers in homogeneous grasslands. Diversity-function studies have manipulated the number (richness) or composition of species or functional groups in the community.

For a comprehensive understanding of the interconnections between plant diversity, plant cover, soil fertility and plant biomass, more studies should be done to probe into these relations and hence make a decision along this path. Plant diversity-biomass relationship, plant cover-biomass is essential and complex [16]. In addition, the highests dry matter yields comparing the two year experiment results, was found in the experiment without synthetic fertilizers use.

# CONCLUSSIONS

For all mixtures almost in all cases higher yields were found in mixtures with legumes and showed better growth properties than monocultures without fertilizers.

Grass monocultures lack nutrients for quality growth, so yields can be increased by using mineral fertilizers or by incorporating legumes that have a similar effect to the used nitrogen fertilizers.

Less investigated sainfoin in mixtures showed better growth properties than white clover only in the first year of sward use. In the second year of grassland growth, the amount of white clover was significantly higher than in the first. Red clover is suitable in mixtures particularly with lucerne. No significant differences were observed between the growth rates of perennial ryegrass and xfestulolium, higher yield were found in the interaction with legume plants.

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# MIDDLE STOREYS OF PIONEER DECIDUOUS TREE STANDS IN FERTILE FORESTS HABITATS. CASE OF LITHUANIA

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#### EXTENDED ABSTRACT

### **OVERVIEW**

Forest ecosystems face challenges of climate change, the pressure of economic activity on biodiversity. As European policies turn Green Deal, ecological forestry systems, which aim to increase or at least not reduce biodiversity while maintaining high forest productivity, are becoming particularly relevant. The basis of ecological forestry is a partial simulation of natural processes in forests. This study examines distribution regularities of middle storeys (second storey; understorey - trees up to 4 m high which could replace the main storey of stand; underbrush - trees and brushes which could not by replace the main stories of stand in current forest sites) in fertile unwet habitats' forest communities of pioneer deciduous tree species, the understanding of which will allow the development of forestry systems that exploit the natural forest regeneration potential. The aim of the study is to find out how the middle storeys of stand pioneer tree species of highly fertile habitats develop in the context of local natural conditions and farming history. What is the prevalence and diversity of the second storey, understorey and underbrush? What are relationships between their indicators?

### METHODS

The study represents forests in the territory of Lithuania. There was used stand-wise forest inventory data (updated in 2019) of *Betula spp.*, *Populus tremula*, *Alnus incana* mature and older stands, which amounts to 153.2 thousand ha. We analyzed how middle storeys are distributed in stands of different tree species according to soil conditions and the age of the stand, the stocking level, and the mixture of species. A cross-tabulation was utilized to analyze the data, chi-square and z tests were used for comparison. A nonparametric Kendall tau-b correlation was used to check the relationship between density and age of stand elements.

### RESULTS

The largest prevalence of 2nd storey was found low in very fertile *Betula* stands, the lowest – in *Alnus incana* (Fig. 1.), *Picea abies* was most frequent tree species of 2nd storey (on average 24.1%), *Tilia cordata* and *Carpinus betulus* was less common. With the increase of stand mixture in the stands of all studied tree species, the frequency of stands without the 2nd storey decreased. We found trends that the frequency of the 2nd storey increases with the age of the stand in some age groups.



Fig. 1. Prevalence of 2nd storey in *Betula spp.*, *Populus tremula* and *Alnus incana* stands of different composition (letters show significant differences: large - between stand of different tree species, small - between stand of different mix;  $\chi 2$ , z-test,  $\alpha = 0.05$ )

The amount of understorey in very fertile soft deciduous stands was very low. *Picea abies* understorey was the most common (on average 8.1%), less *Fraxinus excelsior* (on average 2.7%), other tree species - episodically. The trend in understorey distribution by predominant tree species and stand mix was similar to those in the second storey. Analyzing the distribution of 2nd storey and understoreyvaccording to the forest habitats, it was found that the 2nd storey and understorey is found the least in slopes. Frequency of 2nd storey increases with increasing moisture and fertility of habitats.

Betula and Populus tremula forests were dominated by stands with Corylus avellana underbrush (Fig. 2.). With the increase of stand mixture in Betula stands, the frequency of stands with the predominant Corylus avellana underbrush increases significantly. This tendency is more pronounced than in Populus tremula stands. The predominant species of underbrush in Alnus incana stands was Padus avium. The frequency of dominant Padus avium underbrush decreases significantly with increasing stand mixture.



Fig. 2. Distribution of predominant understorey tree species in *Betula*, *Populus tremula* and *Alnus incana* stands of different composition (letters show significant differences between stand of different mix;  $\chi 2$ , z-test,  $\alpha = 0.05$ )

The predominant Corylus avellana underbrush is significantly more common in the most fertile habitats and the least in slopes. The distribution of Padus avium underbrush was reverse: significantly less

common in the most fertile habitats than in fertile. A high prevalence of dense and medium-density underbrush was found in all types of stands.

Kendall's tau-b correlations show significant linear relationships between indicators of individual stand elements and age. As the age of the stand increases, the stocking level of the first storey decreases, but the stocking level of the second storey increases. The density of the underbrush increases with decreasing the stocking level of the second storey and the stocking level of the first storey.

### CONCLUSIONS

The understorey and the second storey of mature *Betula*, *Populus tremula* and *Alnus incana* stands are weakly forming in most of the very fertile undisturbed habitats. *Picea abies* second storey and understorey are most frequent. As the age and species mixture of stands increase, the understorey and the second storey develop more often. Dense understorey with the predominant *Corylus avellana* is the most common middle storey in *Betula* and *Populus tremula* stands of very fertile habitats. In *Alnus incana* stands of very fertile habitats, *Padus avium* underbrush is the most common and abundant type of middle storey.

**Keywords**: ecological forestry, forest succession, fertile forest type, pioneer tree stands, ecological forestry, temperate hemiboreal forests

# PHYSIOLOGICAL AND METABOLIC RESPONSE INDUCED BY PLANT BIOSTIMULANTS

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### ABSTRACT

Plant biostimulants based on natural materials have received considerable attention from the scientific community and commercial enterprises, especially in the last two decades. Due to changing climate conditions, it is difficult to absorb nutrients from soil effectively. Biostimulants are known for ability to relieve stress as well as to reduce the amount of mineral fertilizers used and intensify plant metabolism, which results in the preservation and conservation of the fertile soil layer. In this aspect, environmentally friendly, sustainable farming and adaptation to climate change are encouraged. Biological and physiological investigations will be carried out enabling to identify new biological molecules, pathways and processes.

Biostimulants affects physiological plant development processes during critical onthogenesis stages: rooting, bud development, flowering or maturity. Besides, by modifying physiological processes with biostimulants both natural plant developmental processes and nutrient uptake are stimulated, allowing to overcome the abiotic stress. This review is focused on classification of biostimulants and current understanding about its effect on plant response to stress, the effects of biostimulants in terms of their action on different regulatory and functional systems of plants will be overviewed.

Keywords: Biostimulants, soil, stress, fertilizers, metabolism, onthogenesis, phytohormones

## **BIOSTIMULANTS IN AGRICULTURE**

One of the most important factor in promoting plant productivity is available nutrients in the soil. However, increased yields and unfavourable meteorological conditions results the complicated nutrient uptake from soil at critical plant development stages, leaving fertilizer costs stable or increasing and productivity poorly predicted. To prevent nutrient deficiencies at critical stages, soluble fertilizers for foliar applications and watering are used, which partially cover the resulting deficiencies, stimulate physiological processes, preventing plants from environmental stress, which usually results in loss of vegetation time, reduced productivity, reduced fertilizer uptake and increased environmental pollution.

This review will focus on current known classification of biostimulants or its coumpounds. However, plant biostimulants can help for a plant adaptation and increase its productivity. As a result, this problem in the last decade received a lot of attention from scientific community and commercial enterprises. In 2019 market of biostimulants reached up to 2.6 bilion USD and it is estimated to reach 4.9 bilion USD by 2025 [1].

By its natural origin, plant biostimulant compounds triggers physiological and molecular processes, which results in higher yield and better quality and increased resistance to pathogens and environmental conditions. Brown [2] hypothesize, that biostimulants help to produce beneficial molecules to the plant through stimulation of bacteria activity or by stimulanting signaling cascades (Figure 1).



Fig 1. Non-lethal stress is experienced by all crops resulting in loss of productivity, according to Brown [2]

# **GENERAL CLASSIFICATION OF BIOSTIMULANTS**

There are various classification of biostimulants proposed by many authors. It is known that one of the first attempt to categorize these substances was suggested by Filatov [3], which split the materials into four different categories, Ikrina and Kolbin [4] divided raw materials into nine. Basak [5] suggested that biostimulants should be categorized by the origin of active ingredient. Unfortunately, there is no legal clarified definition of regulation of plant biostimulants, including European Union and United States Du Jardin [6]. Depending on scientific articles and market supply biostimulant products can be divided into few categories: humic and fulvic acids, seaweed extracts, biofertilizers and protein hydrolysates.

# Humic and fulvic acids

Humic acids are substances, which forms from metabolic activity of soil microbes, decomposing a plant, animal or other microbial residues. According to their molecular weight and solubility these substances are categorized into humins, humic acids and fulvic acids [6]. The effect of humic and fulvic substances depends from environmental conditions, dosage, source of extraction ofhumic substances and application mehod [7]. Regarding sources humic substances are extracted from naturally humified organic matter, composts, vermicomposts or mineral deposits [6]. Biostimulants with humic substances mostly refers to increased root nutrition, nutrient uptake and cation exchange. Another effect of humic substances to root nutrition is stimulation of plasma membrane H<sup>+</sup> ATPases, which converts energy released by ATP into electrochemical potential, which allows import into a cell other important nutrients. As a result plasma membrane ATPases loosens cell wall which contributes cell enlargement and organ growth [8].

### Seaweed extracts

The use of seaweed extracts as a source of organic matter is known for a long time, but only recently biostimulating effects were recorded. Many authors have confirmed positive effect of seaweed extract on crop yields. Legumes positively respond to foliar seaweed applications of seaweed extracts (*Caulerpa racemosa, Ascophyllum nodosum, Ecklonia maxima, Sargassum wightii, Kappaphycus alvarezii*) by increasing number of pods and seeds, one thousand seed weight and yield in soybean [9], chickpea [10], fava bean [11]. Furthermore, studies have showed different origin of seaweed extracts and concentration can influence plant development differently [12]. Foliar applications of *Corallina elongate, Sargassum latifolium* increased height of wheat [13], eggplant [14] and tomato [15]. Also, research on high concentration (100 %) of *Sargassum crassifolium* resulted inhibited growth of tomato [15].

Seaweed can be applied on soils as well as in hydroponics or used as foliar treatments. There has been found, that many bioactive substances, such as phytohormones (cytokinins, auxins, abscisic acid, gibberellins) contains in seaweed extracts [16]. Polysacharides, which also contains in seaweeds, increases water retention and soil aeration. There are also reports about anti-stress and protective effects with seaweed extracts, where regulation of endogenous stress-responsive genes could be involved [17].

## **Exogenous plant hormones**

Biostimulants based on plant hormones could also participate in regulation and optimize plant growth. Previous studies have shown, that by manipulating different exogenous hormones and its concentrations crop growth and tiller bud formation can be promoted or inhibited. Liu [18] has shown that additional application with napthyl acetic acid (NAA) can inhibit growth of tiller buds in rice, while increased cytokinin concentrations can promote it [18]. Moreover, Cai [19] has shown that tiller buds growth was inhibited by applying gibberellic acid (GA<sub>3</sub>). Another studies have also shown, that using zeatin nucleosides (cytokinin) sprouting of tiller buds in maize can be promoted [20]. Exogenous abscisic acid (ABA) can also affect tiller bud growth by increased endogenous ABA content in tiller nodes [21]. An external hormone use has been shown to be an effective tool to regulate bud growth [22].

# **Biofertilizers**

In this review biofertilizers are considered as beneficial fungi and beneficial bacteria, when applied on soil, plants or seed has growth-promoting effect by increasing supply of nutrients, root biomass, root area and nutrient uptake capacity. Fungi interacts with plant roots differently: from symbiotic relationship to parasitism [23]. Mycorrhizal fungi are able to establish symbiotic relationships with over 90 % of plant species and they have a great interest to its effect on symbioses to nutrition efficiency [23] and its ability to form fungal hyphae branched structures called arbuscules [24]. Another difference, distinct from mycorrhizal species, is that *Trichoderma* spp. are able to survive seperately from the plant and after colonizing roots transfer nutrients to their host [23]. Also, this type of fungi has a specific use for biopesticide and biocontrol application and has been extensively studied [25].

Meanwhile, rhizobacteria interact with plant in many ways and its well known for its ability to promote plant growth under low input conditions and can solve some environmental problems [26]. Studies have shown, that plant growth-promoting rhizobacteria (PGPR) increased nitrogen efficiecy of lettuce by improving its uptake under low nitrogen availability conditions [27]. PGPR's affects many aspects of plant life: nutrition, growth, development, response to biotic and abiotic stress. The use of agricultural PGPR is limited by this complexity, the changing responses of plant varieties and the host environment. In addition, the practical

difficulties involved in inoculator formation result in inconsistent results in practice [28; 29]. Nevertheless, the global market for bacterial biostimulants is growing and PGPR inoculants are now considered as certain plant "probiotics" an effective plant nutrition and immunity factors [30].

## Protein hydrolysates and amino acids

Products containing amino acids can be divided into two categories: protein hydrolysates, which contains mixture of peptides and amino acids of plant or animal origin. Mostly these substances are prepared by enzymatic, chemical or thermal hydrolysis [17]. There are various reports about effects of protein-based products and its biostimulating role in plant development [17, 6, 31]. Also, it has been demonstrated that protein hydrolysates plays key role in modulation of plant molecular and physiological processes and triggers growth, increase in yield and has impact dealing with abiotic stress [17, 32]. Furthermore, these substances could also interfere with plant hormones, due to presence of bioactive peptides [33]. Studies have shown, that products obtained from protein hydrolysates participate in hormone-like activities and promoted shoot growth and increased productivity of a crop [34, 33, 35]. Protein hydrolysates also has indirect effect of plants and soils. These substances are known to increase microbial activity and its mass, soil respiration and fertility.

# **MECHANISMS OF ACTION**

Mechanisms of action of a majority of biostimulants are still unknown. The reason is mostly due to materials and its components within biostimulants, which makes difficult to identify the component responsible for the biological activity and the relevant modes of action [36].

Furthermore, multicomponent biostimulants contains measurable but irrelevant concentrations of other nutrients, such as amino acids, plant hormones or other substances which has no effect when used at recommended rates [32].

In order to understand modes and mechanisms of action using biostimulants Yakhin [32] systemized the stages of biostimulant action on plants after application: 1) penetration into tissues, 2) gene expression and signaling, 3) physiological response effects.

# **Penetration into tissues**

Amino acids or protein hydrolysates penetrates into tissues due to diffusion through cell membrane pores, which require energy [37]. Maini [38] in 2006 investigated this process by radiolabeling proline and glycine which contained within biostimulant. Results shown, that these molecules penetrated into tissues rapidly and were transported to other leaves. Biostimulants must be highly soluble in water or other suitable solvents. This is a precondition for many uses and for sufficient penetration of active substances into the internal structures of treated plants [39].

# Gene expression and signaling

In order to fully understand the biological activity of complex biostimulant preparation it will require a deeper understanding of mechanism of action and its effect on plant productivity as well as identification of biologically active molecules and their mode of action [40]. Determining the mode of action of biostimulants is complicated by the observation that many biostimulants stimulate gene activity and increase productivity when plants are dealing with biotic and abiotic stress. Therefore, experimental methods need to be developed to create

appropriate and reproducible stress conditions in order to obtain results that are related to the alleged effects on plant productivity using any molecular tool to study gene function [32].

Plant response to enviroment conditions by signaling molecules has been constantly researched [32]. Signal transmission is a process, which involves synthesis of signaling molecules, its translocation and their binding receptors which results cellular responses [41, 42]. When a receptor binds with its signaling molecule, as a response activates secondary messengers or intracellular signaling mediators. Some bioactive compounds in some biostimulators are also suggested to show plant signal activity or to induce signaling pathways. Protein hydrolysates (amino acids and peptides) acts as signaling molecules in regulation of plant development [34]. For example, it is displayed that protein hydrolysates from soybean and casein acts as elicitors and increases grapevine immunity against *Plasmopara viticola* [43].

### **Physiological response effects**

There are many reports suggesting that biostimulants improve plant productivity, increases assimilation of nitrogen, carbon and sulphur [44], improves photosynthesis and stress response. There are also reports that biostimulants increase amino acids, protein, carbohydrates, phenolic compounds, pigment levels and enzmye activity. Furthermore, protective effect of substances containing biostimulating molecules are associated with stress induced reactive oxygen reduction and activation of plant defense mechanisms against oxidation [45].

Plant biostimulants applied on critical growth stages can increase photosyntesis, metabolism or response of antioxidant systems. Cai [19] has found that exogenous indole-3-acetic acid (IAA) and zeatin applications has impact on tiller bud development. The results showed that additional IAA inhibits occurrence of tillers while zeatin promotes it.

There are reports about exogenous abscisic acid applications on plants during drought stress. Additional abscisic acid (ABA) applications under strees on plants resulted increased IAA and GA content, compared to control [46]. Latif [47] has found that exogenous ABA applications reduced negative effects of drought in *Pisum sativum* plant and ABA phytohormone increased proline and antioxidant enzymes content in plants exposed to drought stress.

However, it is still unclear how biostimulants, containing active small molecular weight compounds, have predictable and benefitial outcome [32].

### **FUTURE PERSPECTIVE**

In developing and improving yields, quality, physiological response and interaction of biostimulants with different environmental stressors, there must be clear concept where biostimulant products stand in these technologies. Due to complex effect of biostimulants a lot of research must be performed regarding photosyntetic, metabolic and antioxidant response problems at critical stages of plant development.

Products containing biostimulants stand as additional tools to help crops to recover after dealing with stress and also, increases absorption and effectiveness of other nutrients containing in soil (Figure 2).



Fig 2. Biostimulants and their place in technology.

The industry of biostimulants faces many problems and challenges. Mostly biostimulants have been developed based on observational data and only few modes and mechanisms of action has been known [48]. Products, containing single active components are easier to describe and determine its effect and register. However, products with more than one active substances are much more difficult to describe and they may offer a solution to biological synergy [49].

Continued investment by commercial operators in biostimulatory research and product development will be a critical engine of discovery in this area and will inevitably help to identify new biological phenomena, pathways and processes that would not be discovered if the biostimulant category were not identified [32].

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# GROWTH PROMOTING EFFECT OF ENDOPHYTIC PAENIBACILLUS SP. ON POPULUS SP. MICRO-SHOOTS IN VITRO

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### EXTENDED ABSTRACT

#### **OVERVIEW**

Biofertilizers are microorganisms that increase nutrient uptake and bioavailability by plants [1]. In recent years, they have gained interest as an alternative way to sustainably increase soil fertility and harvest yields. This method is a potentially effective way to limit the need for chemical fertilizer production and reduce chemical leeching [2].

Endophytes are microorganisms that can most often be found in intercellular spaces and vascular tissues of host plants for at least a part of their life cycle, but do not cause their hosts any harm under normal conditions. They may be beneficial to their host plants both directly and indirectly through a variety of mechanisms [3].

Endophytic bacteria used as biofertilizers can enhance plant nutrient uptake and accessibility through nitrogen fixation, phosphate solubilization and iron transport agent-siderophore production [4,5]. Bacteria can also produce phytohormoes, like indole-3-acetic acid (IAA), which can positively effect affect plant development and growth [6,7]. Thus the use of these biofertilizers could limit and/or eliminate our dependability on chemical fertilization.

English oaks (*Quercus robur*) are model trees from the genus *Quercus*, which is spread all over the Northern Hemisphere [8]. They are key hardwoods, known for supplying food and habitat for multitude of organisms in temperate forests. Oak bark and wood are also notably valuable for various enterprises [9]. Previously oak endophytic fungi have been studied for biocontrol potential against oak pathogens [10-13].

Because of their extensive habitat and long life spans, oaks are valuable as a niche for various beneficial bacteria, that as of yet have not been thoroughly researched. Even though cultivable endophytic bacteria represent just a small fraction of host plant microbiota [12], they are important because they could be applied as biofertilizers and biocontrol agents in forestry enterprises [4,12,14,15].

The aim of this study was to test the effect of English oak (*Q. robur*) endophytic *Paenibacillus* sp. strain on model poplar (*Populus* spp.) tree growth parameters *in vitro*.

### METHODS

#### Isolation and identification

Seven English oaks were tested in this study. Branches were collected at the end of spring and force flushed in the lab. Leaves and buds were used for the isolation cultivable endophytic bacteria strains. They were surface disinfected using a modified method[16]. Leaves and buds were removed from the branches and washed in a Tween 80 detergent solution (1 drop/125 ml dd H2O) for 5 minutes, then in 50% strength commercial bleach solution with dd H2O for 2 minutes. The last wash cycle was done using 80% ethanol for 40 seconds. After each wash, explants were washed with dd H2O 3 times, 2 minutes each.

Surface desinfection efficacy was tested using a modified method by Hoffman et al. [17]. Explants were gently pressed against Woody plant medium (WPM) (Duchefa Biochemie, The Netherlands) [18]. If no microbial growth was discerned in a month, the surface disinfection was successful. These explants were later used for the

isolation of endophytic bacteria. At this point explants were cut into smaler pieces to promote bacterial spread and growth and placed onto fresh WPM.

After 1 week different putative bacterial morphotypes were selected and transferred from WPM onto Lysogeny broth (LB) agar [19] (Duchefa Biochemie). Samples were grown at room temperature in a growth chamber. Quadrand streaking method was used to achieve pure cultures.

Based on colony morphology, the most abundant bacterial morphotype was sent to Microgen sequencing center (The Netherlands) for DNA extraction and 16S rRNA gene sequencing.

#### **Micro-shoot inoculation**

The effect of one isolate was assessed on tree growth parameters in vitro. For this, 2 different poplar (Populus) micro-shoot cultures were selected: Populus tremula and a hybrid of P. tremula x P. alba. Per a modified method described by Ulrich et al. [20], for the uninoculated groups, 30 explants from each 2-month-old poplar micro-shoot culture were used. Micro-shoot leaves were removed and the stems were cut into 10mm sized segments, each with 2-3 nodes. Each segment was placed into glass tube (Ø20mm) with 5,25ml of WPM (4% gelrite, 2% sucrose). Micro-shoots were grown in a growth chamber at room temperature with 16/8h light cycles.

For the explant group that were inoculated, the bacterial colonies had to be prepared first. A sample from a single bacterial colony was relocated to a fresh plate with LB medium and grown at room temperature overnight. Prior to the transfer of micro-shoot segments, each tube was inoculated using a sample from 24h old prie-prepared bacterial colonies using an inoculation needle. Then micro-shoot segments were placed into the stab area.

After 2 months of incubation, various growth parameters were measured: width of the largest leaf, lateral root number, shoot number and length, adventitious root number and length, fresh and dry biomass weight, lateral root density. Student's t-test and ANOVA were used for statystical analysis.

### **IAA production**

Based on the results of the inoculation study, we checked if the selected bacterium was capable of tryptophan-dependent IAA production. Bacteria were grown in LB broth (Duchefa Biochemie) with added tryptophan (0.15% w/v) in a thermalshaker (lowest setting) at 25°C in the dark for 24 hours. Afterwards 1.5ml of the suspension was moved to a Ependorf tube and centrifuged for 5 minutes at 16300 x g. Subsequently, 0.5ml of the supernatant was transferred to a cuvette and Salkowski reagent (1ml 0.5M FeCl3 with 49ml of 35% HClO4 v/v) 1:1 was added on. The cuvettes were incubated for half an hour in the dark. Then using T80+ UV/VIS Spectrophotometer (PG Instruments LTD, UK) optical density was measured at 530nm. Uninoculated LB broth with tryptophan (0.15% w/v) and Salkowski reagent 1:1 were used as control. IAA production was estimated based on the standard curve and color change from yellow to red [21].

#### RESULTS

In this study, we assessed biofertilization capabilities of cultivable bacterial endophytes associated with English oak. After surface sterilization putative bacterial endophytes created visible colonies on the medium surface within few weeks. In total 50 viable bacterial samples were isolated. Forty percent of them had the same colony morphology. A partial 16S rRNA gene of this morphotype was sequenced (1484 bp).

The isolate was shown to belong to phyla Firmicutes. It was homologically closest with Paenibacillus tundrae (NR\_044525.1, % Identity - 99.39%, Query coverage – 99%). Its morphotype was found in almost all of the individuals tested. In later tests this isolate was shown to produce IAA from tryptophan, on average at  $27\pm0.002$  µg/ml after 24h incubation.

After incubation (2 months), the results of inoculation with Paenibacillus sp. had a statistically significant positive effect on the root development of both P.tremula and P.tremula x P.alba hybrid micro-shoots. Analysis of variance revealed that on average inoculated P. tremula micro-shoots had increased lateral root number by 44.7% ( $p\leq0.01$ ), lateral root density by 66% ( $p\leq0.0001$ ), fresh and dry root biomass by 101.9% ( $p\leq0.0001$ ) and 63.6% respectively ( $p\leq0.001$ ).

On average in P. tremula x P. alba hybrid, it also positively affected lateral root number and density, it increased by 213.7% ( $p\leq0.0001$ ) and 125.6% ( $p\leq0.001$ ) respectively. Additionaly, root biomass, both fresh and dry, increased by 197.1% ( $p\leq0.01$ ) and 144.8% ( $p\leq0.001$ ) respectively. Adventitious roots of this genotype were also significantly affected. Sum length of adventitious roots was enhanced by 102% ( $p\leq0.0001$ ) (longest adventitious root length increased by 79.5% ( $p\leq0.001$ )). Adventitous root numbers were also higher by 65% ( $p\leq0.01$ ). Inoculation had a negative effect on aboveground fresh biomass, it droped by 25% ( $p\leq0.01$ ).

#### CONCLUSIONS

We report that *Paenibacillus* sp. (homologous with *P. tundrae*) was for the first time isolated from *Q. robur* leaf endosphere. It was capable of tryptophan dependent IAA production. Poplar micro-shoot inoculation study revealed that *Paenibacillus* sp. isolate inoculated micro-shoots of two different genotypes had a significant positive increase in their root growth and development. Our results suggest that this bacterium may potentially be used as a biofertilizer, though further research is required.

Keywords: endophytes, Paenibacillus, Populus, plant growth promotion, Quercus robur

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# PHENOTYPIC DIVERSITY AND HARMFULNESS TO WHEAT OF FUSARIUM SPECIES RESIDING IN NON-GRAMINEOUS PLANTS

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### ABSTRACT

Fusarium head blight (FHB) is a very common wheat disease of devastating impact and global importance in recent years. FHB is mostly associated with Fusarium species, most of which are potential trichothecene producers. So far, most studies have focused on small grain cereal as hostplant of this pathogens, but recently it has been found that several species of non-gramineous plants can serve as asymptomatic alternative hostplants and harbor with FHB associated Fusarium fungi. Despite studies demonstrating the extensive adaptation of Fusarium species to reside in the internal tissues of various agroecosystem plants, it is still difficult to understand the true role of F. graminearum and other Fusarium species in FHB epidemiology, as morphologically and genetically distinct Fusarium species may have high phenotypic diversity. Even though a lot of research is already done in investigating Fusarium spp. and it is known that Fusarium graminearum residing in alternative host plants can be pathogenic to wheats, yet the true importance of the other Fusarium species still remains unclear. It is therefore necessary to investigate the ability of asymptomatically existing *Fusarium* species to cause FHB symptoms in cereals, to determine whether these species are more aggressive to wheats and resistant to fungicides than those from the primary hosts. The aim of this study is to investigate the diversity of the population of common Fusarium species in different alternative hostplants according to phenotypic traits, which include pathogenicity to wheat, sensitivity to fungicides and ability of F. graminearum to form the teleomorphic stage on hostplants residues in vitro. Only broader studies of Fusarium fungi residing in alternative plants would help to understand the FHB epidemiology and it would be more possible to mitigate the spread of the disease.

Keywords: Fusarium, non-gramineous, perithecium, wheat pathogen, fungicides, weed.

### LITERATURE REVIEW

#### Introduction

Food safety and quality are important issues for a rapidly growing human population. Over the last decade, the rapid growth of human populations, soil degradation, global climate change have affected food production systems, resulting in increased demand for grain. Wheat (*Triticum aestivum* L.) is one of the most important small-grain cereal in the world, with an annual production of about 761.7 million tonnes [1]. In Lithuania, wheat is the main cereal crop, occupying about 59% (896.2 thousand ha) of the total cereal growing area [2].

Wheat and other small-grain cereal disease - Fusarium head blight (FHB), mainly caused by several *Fusarium* species or their complexes, has received considerable attention in recent decades. Although much effort has been put into combating FHB in recent decades, the disease remains one of the most important and widely studied diseases of wheat and other cereal plants [3]. This disease is a major concern worldwide, as it can cause up to 60% loss in grain yields [4]. In the past, FHB and the resulting yield losses posed a minimal threat to farmers in Lithuania. The first outbreaks of this disease were observed only in 2012, but since then FHB has remained as a serious problem in Lithuanian fields [5,6].

Species belonging to the genus of *Fusarium* are present everywhere: in soil, air, water, plants, and animals. Depending on the need for ecological conditions, soil-borne *Fusarium* species can be parasites, endophytes, or pathogens [7]. *Fusarium* spp. survives well as

saprophytes on plant debris, or can survive on plant surfaces without causing disease [8]. Under favorable environmental conditions for the spread of FHB, fungi of this genus can turn into destructive opportunistic pathogens with a relatively narrow infection window. The development of resistant cereal varieties plays a crucial role in the effective and reliable control of FHB, but at the epidemic conditions, even the most effective fungicides may not be good enough to keep toxin levels below critical levels, especially for sensitive varieties [9,10].

To date, most studies have focused on the main hosts of Fusarium pathogens, but it has been found that many of non-gramineous plants (especially weeds) present in agroecosystems or wild plants surounding the fields can serve as asymptomatic alternative plants inhabiting FHB-associated Fusarium species. Recently conducted studies in Lithuania confirmed, that F. graminearum residing in non-gramineous plants (oilseed rapes, potatos, sugar beets and peas) and weeds (41 species) are pathogenic to spring wheat but the effects of other Fusarium species in the FHB manifestation remained unclear [11,12]. A number of studies demonstrate the extensive adaptation of *Fusarium* species to colonise the internal tissues of various agroecosystem plants, however it is still difficult fully to understand the true role of F. graminearum and other Fusarium species in FHB epidemiology, as morphologically and genetically distinct Fusarium species may have high phenotypic diversity [13]. It is therefore necessary to investigate the ability of asymptomatically existing *Fusarium* species (especially other than F. graminearum) in alternative hosts to cause FHB symptoms in cereals, to determine whether these species are more aggressive to wheats and resistant to fungicides than those from the primary hosts and ability of F. graminearum to form the teleomorphic stage on alternative host-plant residues.

## Fusarium pathogenicity to wheat

It is known, that *Fusarium* spp. is considered as pathogenic fungi because of its ability to cause harmful diseases such as crown, fruit, root, stem and stalk rots, head blight to various plants [14]. In gramineous plants Fusarium species such as F. graminearum, F. avenaceum, F. culmorum, F. poae, F. sporotrichioides, F. tricinctum, F. langsethiae causes Fusarium head blight (FHB) [15,16,6]. and such species as F. culmorum, F. poae and F. pseudo-graminearum - crown rot (CR) [17]. Yield losses due to FHB rank second after leaf rust disease and are particularly prevalent in China, the U.S. Midwest, Canada, Southern Brazil, Paraguay, Uruguay, and Argentina [4]. These pathogenic fungi cause a great concern since they not only reduce yield, but it also contaminate cereals with harmful mycotoxins. Mycotoxins produced by fungi of the genus Fusarium are very widespread and have great economic importance in terms of their toxicity to animals, humans and other plant pathogens [18]. Among the mycotoxin-producing species the most aggressive and harmful are F. graminearum, F. culmorum, which synthesize the type B trichothecenes, such as deoxynivalenol (DON) and its acetyl forms (15 acetyldeoxynivalenol 15ADON and 3 acetyldeoxynivalenol 3ADON) and nivalenol [19]. F. avenaceum synthesizes beauvericin, enniatin and moniliformin [20,21]. Many mycotoxins remain stable during food processing, they are generally resistant to chemical and thermal effects [22,23].

Wheat (*Triticum aestivum*), barley (*Hordeum jubatum*), rice (*Oryza sativa*), oats (*Avena sativa*), rye (*Secale cereale*), triticale (*Triticum secale*) and maize (*Zea mays*) are the main primary host plants of pathogenic *Fusarium* spp. However weeds and wild plants around the fields as well as non-gramineous plants can be alternative hosts for pathogens, thereby increasing disease incidence in associated crop plants [24]. In recent decades, scientists have increased their attention to investigate of *Fusarium* spp. residing in weeds and non-gramineous plants. Several assays have shown that asymptomatic and broadleaf weeds, as well as wild grasses, are reservoirs to *Fusarium* spp. related to harmful diseases of gramineous cereals

[25,26]. Ilic et al., in their research investigated pathogenicity of thirty isolates (from weeds and plant debris in eastern Croatia) representing 14 *Fusarium* species on wheat and maize seedlings [27]. All tested *Fusarium* spp. isolates were pathogenic to wheat seedlings and the disease index was statistically significantly higher than the disease index comparing to control. Pathogenicity of *Fusarium* isolates for wheat seedlings differed between species and strains: *F. graminearum* isolated from *Amaranthus retroflexus* and *Abutilon theophrasti* were most pathogenic with disease index (DI) 100.0, while *F. graminearum* from *Chenopodium album*, two isolates of *F. sporotrichioides* from maize debris and *F. avenaceum* from *Agrostemma githago* were less pathogenic (DI 77.5; 76.0; 80.0 and 60.0 respectivelly). In another study have been found, that isolates of *F. graminearum* isolated from potato and sugar beet cause symptoms of FHB in wheat and produce different mycotoxins in wheat spikes and rice grains [28,29].

Recently conducted studies in Lithuania demonstrated that oilseed rape, potatoes, sugar beet, peas, and 56 weeds species (all detected in the field) were asymtomatically colonised by nine *Fusarium* species: *F. avenaceum*, *F. culmorum*, *F. graminearum*, *F. equiseti*, *F. tricinctum*, *F. sporotrichioides*, *F. poae*, *F. oxysporum* and *F. redolens* [11,12,13] on pathogenicity tests, all tested *F. graminearum* (91 isolates) were able to cause FHB symptoms in spring wheat and the disease severity values were comparable to those isolated from primary host plants - wheat and barley. Primary results of study conducted in 2019 showed that *F. culmorum* isolates from asymptomatic weeds and non-gramineous plants posed similar affect to spring wheat as *F. graminearum*, however the role of others *Fusarium* spp. in the epidemiology of the FHB remained unclear [30]. Previously similar findings were made by Pereyra and Dill-Macky, who indicated that *F. graminearum* isolated from *Digitaria sanguinalis* residues caused FHB in wheat and barley [25].

A review of previous studies suggests that altogether non-gramineous plants and weed species can be considered as reservoirs of pathogenic *Fusarium* spp. and sources of inoculum, leading to spread of FHB and other with *Fusarium* associated diseases. In addition, it is evident that further exploration are still necessary for pathogenicity of *Fusarium* species most commonly associated with FHB. Particular attention should be paid to *Fusarium* fungi residing in alternative host plants and to determination whether these pathogens are more aggressive than those derived from the primary hosts.

## Fusarium susceptibility to fungicides

Another important issue in the evaluation of plant pathogens is their susceptibility to fungicides. The use of fungicides is one of the strategies to manage FHB and DON. The most widely used fungicides belong to demethylation inhibitors (DMIs) class [31]. They include metconazole, propiconazole, tebuconazole, prothioconazole and prothioconazole + tebuconazole. A meta - analysis of fungicide studies in the United States showed that prothioconazole + tebuconazole, metconazole, and prothioconazole were superior to propiconazole and tebuconazole in inhibiting FHB and DON, and all five fungicides significantly increased yield and weight in 2008 and reduced FHB and DON [32,33]. Although DMI-class fungicides inhibit FHB and DON, they do not achieve complete control and FHB may continue to spread. On the other hand, the studies shows that a class of QoI (quinone external inhibitors) fungicides including strobilurins may increase DON accumulation, although they partially control the incidence of FHB [34]. Unfortunately, the overall effect of fungicides on FHB control was limited and results are variable.

Orina et al., evaluated four fungicides at four concentrations of active substance (10, 100, 1,000 and 10,000 ppb) in the *in vitro* study with 10 *Fusarium* spp. strains grown in liquid Czapek medium [35]. The tested fungicides included: 1) 50 g/L of imazalil, 40 g/L of metalaxyl, 30 g/L tebuconazole (IMT), 2) 200 g/L of pyraclostrobin 3) 25 g/L of fludioxonil

and 4) 400 g/L of thiram. High concentration of active substance of all fungicides (1,000 and 10,000 ppb) reduced the growth of all fungal strains. The exception was fludioxonil, which did not have any impact on *F. oxysporum*, *F. proliferatum*, *F. solani*, and *F. verticillioides* strains. *F. acuminatum*, *F. equiseti*, *F. semitectum*, and *F. sporotrichioides* strains showed an average level of sensitivity to the fungicides (IC50 13-3523 ppb). *F. culmorum* and *F. graminearum* strains were most sensitive to fungicides (IC50 58-1445 ppb), among which fungicide fludioxonil was the most effective. Overall, the fungicide IMT was the most effective and limited the growth of all ten strains belong to different *Fusarium* species [35].

*In vitro* studies performed in Lithuania showed that isolates of *F. graminearum* 3ADON, 15ADON and NIV trichothecene genotypes isolated from spring wheat were the most sensitive to metconazole, the most resistant to tebuconazole and the susceptibility to prothioconazole was intermediate. 15ADON chemotype isolates were more resistant to all fungicides studied comparing to 3ADON chemotype isolates [36].

Previous studies failed the information on fungicide resistance of *Fusarium* fungi residing in alternative host plants, including even the most common species of *Fusarium - F*. *avenaceum*, *F. culmorum*, *F. graminearum* and *F. sporotrichioides*. Therefore, it is important to draw the attention to this gap and investigate the susceptibility, of *Fusarium* species/strains recovered from alternative plant hosts to at least for most promising fungicides. It is important to determine the impact fungicides on growth of mycelium, spore germination and structural changes of mycelium and spore.

## Ability of F. graminearum to form teleomorphic structures on plant residues

It is known that wheat spikes are particularly susceptible to infection during flowering [9]. *Fusarium* spp. are overwintering on soil crop residues and, depending on the stage of the fungus, produses the sexual (ascospores) or asexual (conidia) spores - inoculum for the onset of FHB [37,38]. These fungi can survive in soil crop residues as saprophytes for up to 2 or more years. Although both ascospores and conidia can be detected in cereal crops, ascospores are more common than conidia in many locations [37]. This is because conidia are produced in sporodochia and are scattered over short distances during rain, while sexual spores (ascospores) mature in the perithecium of the fungus and are released into the air with little force, thus being able to travel kilometers [39]. Sexually impaired holomorphic *F. graminearum/Gibberella zeae* and *F. avenaceum/G. avenacea* is significantly more often isolated from damaged cereals. *F. graminearum/G. zeae* perithecium density and the number of ascospores in them are highly dependent on the plant tissues in which they are formed: the number of ascospores is more abundant in maize residues and less in barley and wheat [25,40].

During the research, conducted by Dill-Macky and Jones was shown that previous plant residues has great impact on *Fusarium* spp. perithecial formation and manifestation of FHB [40]. The results in this research showed that predominant species isolated from corn and wheat was *F. graminearum*, however *F. sporotrichioides* was mostly recovered from the soybean residues. Another research conducted in Uruguay by Pereyra and Dill-Macky investigated presence of *Fusarium* spp. in different plant residues, including wheat, barley, corn, sunflower, fescue, and gramineous weeds species [25]. The results showed, that *Gibberella zeae* recovered on mentioned cropping systems plants including the gramineous weeds *Digitaria sanguinalis*, *Setaria* spp., *Lolium multiflorum*, and *Cynodon dactylon*.

Extremely abundant infection was formed by *Gibberella zeae* in maize residues and brought significant losses to the wheat grown after it [41,42]. Studies in Croatia have found that most *Fusarium* fungi were also found on maize (35%) and less on wheat (15%), oats (2.4%) and sunflower (0.7%) derbis [26]. The formation of ascospores in the residues of alternative

host plants has so far been very little studied, and they are thought to be much less suitable for overwintering and spreading *F. graminearum* than cereals [25,40].

Nevertheless, that in the studies described above, it has already been found that *F*. *graminearum* may form perithecia on alternative host plants residues, it is still not clear whether different *F*. *graminearum* strains are able to develop teleomorphic structures and survive on all alternative host plants occurring in agroecosystems.

# CONCLUSIONS

There are a lot of researches already done in investigating *Fusarium* spp., its epidemiology and pathogenicity to wheat. Most scientists investigated wheat and other gramineous plants as the main host plants of these pathogenic fungi. Whereas insufficient number of research has yet been carried out to investigate the role of *Fusarium* spp. isolated from alternative plant hosts in the epidemiology of FHB. It is known, that *Fusarium graminearum* residing in alternative host plants can be pathogenic to wheats, but the real role of the other *Fusarium* species still remains unclear. Therefore, it is very important to determine whether *Fusarium* species / strains from alternative host plants are more aggressive to wheats and resistant to fungicides than those from the primary hosts. Moreover, it is necessary to investigate the ability of *symptomatic Fusarium* species to cause FHB symptoms in cereals as well as to determine the ability of *F. graminearum* to form teleomorphic structures on host plants residues *in vitro*. Only broader studies of *Fusarium* fungi residing in alternative plants would help to understand the FHB epidemiology and it would be more possible to mitigate the spread of the disease.

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# IMPROVE UREA USE EFFICIENCY BY USING UREA POTASSIUM HUMATE IN SOIL INCUBATION TEST

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#### EXTENDED ABSTRACT

#### **OVERVIEW**

Urea plays a vital role in plant nutrition and soil fertility as a rich fertilizer in Nitrogen (46% N) but if it was compared to other fertilizers of N, it had been considered to be less effective, due to N loss by ammonia volatilization, especially when used on high pH soils or low CEC [1,2]. As well as, urea fertilizers are highly soluble, and once applied to the soil, they may be lost from the soil-plant system or be unavailable to the plants through the processes of leaching, denitrification, immobilization, and fixation in the soil solids as NH4 - N form [3]. The N recovery by crops from soluble N fertilizers such as urea is often as low as 30 - 40%, with a high potential environmental cost associated with N losses via NH3 volatilization, NO3- leaching, and N2O emission to the atmosphere [4]. Also, the loss of nitrogen through ammonia volatilization from surface-applied urea is a vital environmental problem because it is affected by the soil and climatic conditions. Thus, understanding the factors that influence volatilization will enable urea users to select management practices that minimize volatilization. This will increase the quantity of applied N recovered by the crop as well as improving production efficiency and reduce potential impacts of N use on the environment [5]. Therefore, to improve urea - N recovery and reduce its loss, many forms of slow-release urea fertilizers have been developed and applied to different plant species under a range of environmental conditions. The products may be coated, chemically and biochemically modified, or are granular [6]. In addition to address the problems of urea loss, many technological interventions, especially those geared towards the use of certain compounds, such as the organic combination of Humic acid (HA) and urea can form stable chemical bonds, which decreases the nitrogen release rate and increases use efficiency of fertilizer by crops [7]. The application of HA - N significantly raised crop yield, promoted nitrogen absorption and accumulation by crops, and increased Nitrogen use efficiency (NUE) [8]. So, to achieve a balance between profitable crop production and minimizing Urea loss to the environment the main aim of this research is to reduce Urea's Nitrogen loss and improve Urea use efficiency as fertilizer by using Urea Potassium Humate (Urea + PH).

### **METHODS**

The experiment was carried out using 10-liter soil incubation pots, filled with 10 kg of air-dried sandy soil, which grounded to pass 2 mm sieve, mixed with urea fertilizers, and wetted-up using de-ionized water. Soil Pots were into two groups ( $G_1$  = Urea and  $G_2$  = Urea + PH) and three treatments ( $T_0$  = without fertilizer (Control),  $T_1$  = 100 kg N ha<sup>-1</sup> and  $T_2$  = 200 kg N ha<sup>-1</sup>) with 3 replicates of each treatment. The chamber's temperature was adjusted to be constant at 20±2°C and moisture content was replenished regularly by adding de-ionized water to the incubation pots on a mass basis. The soil samples were taken during 35-day incubation period, for mineral N determination (ammonium NH<sub>4</sub><sup>+</sup> and nitrate NO<sub>3</sub><sup>-</sup>) for 1, 2, 3, 4, 7, 10, 14, 21, 28 and 35 days to assess soil mineral nitrogen changes. Mineral Nitrogen and its forms (ammonium NH<sub>4</sub><sup>+</sup> and nitrate NO<sub>3</sub><sup>-</sup>) determine according to LVP D-05: 2016-6 edition, with Spectrometric flow injection analysis (FIA) method, developed by the Agrochemical Research Laboratory.

#### RESULTS
According to some pre studies to study the release of mineral nitrogen and its forms (NO<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup>) from urea granules in the soil is shown in Fig. 1. The process of Nitrogen release has divided to 3 stages: 1) Low concentration; 2) Increase of the concentration; 3) Stability of the concentration.



Fig.1. The Process of mineral Nitrogen release from urea granules as a relation between the concentration of mineral nitrogen forms ( $NO_3^-$  and  $NH_4^+$ ) and Time in Sandy soil during the incubation test.

Also, the results showed that, during the incubation test, the mineral N concentration was increasing with time because of Urea and Urea + PH granules decomposition for all treatments as showen in Fig. 2. Also,  $NH_4^+$  concentration was higher in the Urea group compared to the Urea + PH group with more ammonia losses, then transforms into a low concentration of  $NO_3^-$  form and increased with time. In summary, the mineral nitrogen release rate tends to be slower using urea potassium humate granules compared to urea granules only, this may be due to a higher nitrogen release rate in the  $NO_3^-$  form compared to  $NH_4^+$  form. These findings recommend Urea Potassium humate as an efficient nitrogen fertilizer with less ammonia Nitrogen losses.



Fig. 2. The relation between the concentration of Mineral Nitrogen mg kg<sup>-1</sup> and Time (days) in Sandy soil during the incubation test period.

#### CONCLUSIONS

The results showed that, during the incubation test, the mineral N and its forms (NO<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup>) concentration was increasing with the time as a result of Urea and Urea + PH granules decomposition for all treatments. Also, NH<sub>4</sub><sup>+</sup> concentration was higher in the Urea compared to the Urea + PH, till the end of the incubation that's indicated that the rate of the mineral Nitrogen release is very rapid compared to the Urea + PH group but with more ammonia losses which loss by volatilization. The transformation of mineral N by using Urea Potassium humate was toward transforming the NH<sub>4</sub><sup>+</sup> to the NO<sub>3</sub><sup>-</sup> to improve the use efficiency of the Urea fertilizer by mixing Humic Acid compounds which was the case in the present study. These findings recommend Urea Potassium humate as an efficient nitrogen fertilizer with less ammonia Nitrogen losses.

Keywords: Urea Use Efficiency, Incubation, Nitrogen Loss, Potassium Humate

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# INFLUENCE OF DIFFERENT RATES OF NITROGEN FERTILIZERS ON THE CHANGES OF AMMONIA AND NITRATE NITROGEN CONTENT IN THE SOIL IN WINTER WHEAT

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#### ABSTRACT

In 2019-2020, at LAMMC Rumokai experimental station, studies were carried out to investigate the effect of nitrogen fertilizers on the concentration of mineral nitrogen  $(N_{min})$  in the soil of winter wheat 'Janne' crop. The soil was calcaric luvisol, the granulometric composition was a silt loam on clay. The soil was fertile and rich in nutrients. In the arable layer the pH prevailed in the range of 6.4-5,9, the amount of mobile phosphorus was 148 - 165 mg kg-<sup>1</sup>, mobile potassium - 200-216 mg kg-<sup>1</sup>. After the renewal of winter wheat vegetation in the spring mineral nitrogen (N<sub>min</sub>) was found in the range of 13,2-24,4 kg ha-<sup>1</sup> in the 0-60 cm layer of the soil and the amount of mineral sulfur (S<sub>min</sub>) was 6.0-9.5 kg ha-1 in the same layer of the soil. In April, (Nmin) concentration in the 0-60 cm layer averaged 13.2 mg kg<sup>-1</sup>. According to the two-year data, after fertilization with nitrogen of (N) 0, 45, 105 (60 + 45), 165 (90 + 45 + 30) and 225 (120 + 60 + 45) rates, at the beginning of June, ( $N_{min}$ ) concentrations in soil of winter wheat at BBCH 65 were 6.08, 7.51, 10.91, 16.10 and 25.62 mg kg-1 respectively and can be expressed by the equation  $y = 148,76 \ln(x)-251,66 (R^2 = 0,98)$ . There was not much change in these concentrations in the soil after the winter wheat harvest in early August. This shows that the rates of 165 kg ha-1 and, especially 225 kg ha-1 of nitrogen (N) fertilizers in the 0-60 cm layer of the soil significantly increase the concentration of Nmin, mainly nitrate nitrogen. This potentially increases the risk of nitrate leaching, as the extra yields obtained by fertilizing with these nitrogen rates were small compared to 105 kg ha-<sup>1</sup> rate and was 7.1 and 6.1% respectively.

Keywords: nitrogen fertilizers, mineral nitrogen, yield, grain quality.

## **INTRODUCTION**

Nitrogen (N) is considered as one of the most important plant macronutrients and proper management of N therefore is a pre-requisite for modern agriculture (K.Bergera et al. 2020) The problem of unproductive nitrogen losses from fertilizers is relevant worldwide. Scientific articles state that, on average, plants can absorb 40% of nitrogen in the fields, in some cases nitrogen absorbtion can reach 50-60%. On average, 20-30 percent nitrogen is immobilized in the soil. Nitrogen losses from the soil have a negative impact on the biosphere - soil, groundwater, atmosphere, plants, and through them humans and animals. Nitrogen compounds are involved in causing the greenhouse effect and depleting the ozone layer. In some cases, chemical fertilizers can endanger soil properties and, consequently, human health. The efficient use of nitrogen (N) fertilizers offers great potential for reducing nitrogen oxide (N2O) emissions from greenhouse gases. However, such potential is rarely achieved, as the understanding of what practices (or combinations of practices) lead to reductions in N2O emissions without compromising crop yields is still not entirely clear. Increasing the efficiency of the use of nitrogen fertilizers by using the necessary fertilization rates and the time of their delivery to plants can improve or even solve the problems related to environmental pollution with nitrogen compounds without reducing plant productivity. Optimization of nitrogen fertilization of winter wheat is one of the topical issues of its cultivation (Malhi et al., 2011; Vagusevičienė et al., 2012). A lengthy growth period of these plants is about 10 months, a third of which is characterized by intensive growth of plant mass. Therefore, it is important to distribute nitrogen fertilizers correctly for them during the growing season (Šiuliauskas, 2015; Morari et al., 2021).

According to trials and production experience, winter wheat is fertilized at a rate of 30 kg ha<sup>-1</sup> nitrogen (N) in autumn or not fertilized, if the soil is well cultivated or rich in mineral (N<sub>min</sub>) nitrogen (Smalstiene et al., 2017; Kant et al., 2011). According to the data of the last five years regarding the winter wheat growth in spring in the south-eastern part of the Baltic Sea basin, it resumes in late March- early April; and starting from this period until the end of May, the total remaining rate of nitrogen fertilizer must be applied in two or three splits (Adomaitis et al., 2013; Čermák et al., 2009). It is usually calculated for a grain yield of 6–10 t ha and contains 150–240 kg ha<sup>-1</sup> nitrogen (N), while assessing soil and variety properties (Čermák et al., 2009; Zhuanyun et al., 2020). However, experiments show that a lower rate of 140–180 nitrogen (N), which is applied in several splits, is usually sufficient (Staugaitis et al., 2014; Tian et al., 2018). The nitrogen rate is reduced for several reasons. Firstly, nitrogen is required less than estimated for the planned yield as high amounts of mineral nitrogen in soil are replenished in summer due to mineralization of plant residues (Staugaitis et al., 2014). Secondly, at the end of summer, after winter wheat harvesting, areas with higher levels of nitrogen fertilization remain rich in nitrate nitrogen, which leaches into deeper layers during autumn-winter months, thus polluting groundwater (Cao et al., 2014; Chen et al., 2014). Nitrogen fertilization recommendations and legal documents from various countries generally suggest that winter wheat fertilization should not exceed 210 kg ha<sup>-1</sup> during the growing season, and more than 60 kg ha<sup>-1</sup> of the nitrogen (N) rate per split (Staugaitis et al., 2015; Tedone et al., 2018). Nitrogen rates recommended by various researchers are spread over a wide range, due to soil, cultivated varieties and the agrotechniques used, as well as geographical area, climatic conditions, etc. (Adomaitis et al., 2013; Staugaitis, Vaišvila, 2019).

Mineral nitrogen is mostly leached from the soil in the form of nitrates  $(N-NO_3)$ , even up to 90-98%. In the ammoniacal  $(N-NH_4)$  and nitrite  $(N-NO_2)$  forms, nitrogen is leached out in very small amounts (Adomaitis et al., 2010). It is therefore important to determine the dependence of these forms of nitrogen accumulation in the soil on the amount of fertilizer.

The aim of the experiment was to determine the influence of different rates of nitrogen fertilizers on the changes of ammonia and nitrate nitrogen content in the soil in winter wheat crop.

## MATERIALS AND METHODS

The experiment was performed at the Rumokai Experimental Station of the Lithuanian Research Centre for Agriculture and Forestry in 2018–2020. Winter wheat (Triticum aestivum L.) cultivar 'Janne' was growing, it was sown on 11 09 2018 and 18 09 2019. Winter wheat was fertilised at the rate of  $N_{15}P_{63}K_{108}$  in autumn before sowing in the experimental plot. Complex fertiliser NPK 5-21-36 was used, treatment rate -300 kg ha<sup>-1</sup>. In autumn and spring, the winter wheat in that plot was fertilised with nitrogen (N) kg ha<sup>-1</sup> according to the following scheme: 1)  $N_{15}$  (control), 2)  $N_{60(15+45)}$ , 3)  $N_{120(15+60+45)}$ , 4)  $N_{180(15+90+45+30)}$  and 5)  $N_{240(15+120+45+60)}$ . Fertilisation time and amount of fertiliser were selected taking into account the rate of fertiliser and plant physiology: in the autumn before sowing all variants are fertilised with the same low N<sub>15</sub> rate, to have balanced fertilisation in autumn P<sub>63</sub>K<sub>108</sub> were fertilised to all variants, 50% of the N fertiliser is applied after regeneration of vegetation, the rest is applied in 1-2 times afterwards, rates are split into 1, 2 or 3 applications to avoid leaching and evaporation as much as possible. The plants were fertilised in spring following the renewed vegetation at growth stage BBCH 25-27 (tillering phase), for the second time at BBCH 30-31 (beginning of the stem elongation), and for the third time at BBCH 39 (flag leaf stage). Ammonium nitrate was used for fertilisation.

Soil samples for agrochemical analyses from winter wheat crops were taken three times a year. The sampling was carried out first after plant growth resumption in early spring at BBCH 25 (02 04 2020 and 18 03 2020). PH, plant available phosphorus (P<sub>2</sub>O<sub>5</sub>) and plant available potassium (K<sub>2</sub>O), as well as humus were determined in the 0–20 cm layer. Mineral nitrogen (N<sub>min</sub>), i.e., N-NO<sub>3</sub>, N-NH<sub>4</sub> and their sum were determined in the 0–30 and 30–60 cm layers. Only N<sub>min</sub> was tested for the second and third time; it was determined at winter wheat growth stage BBCH 65 (03 06 2019 and 17 06 2020) and during harvesting. For the first time, before nitrogen fertilisation, soil samples were collected from replications 1, 2 and 3 of the experimental area, where one composite sample from a 0-20 cm layer consisted of 20 subsamples, and composite samples from 0-30 and 30-60 cm soil layers consisted of 9 subsamples. The composite soil samples during the second and third sampling were taken from replications 1 and 3 of each plot. Soil pH<sub>KCl</sub> was determined in 1 M KCl extraction using potentiometric method (ISO 10390), ratio 1:5, P<sub>2</sub>O<sub>5</sub> and K<sub>2</sub>O – by the Egner-Riehm-Domingo (A-L) method, humus - using a carbon analyser after dry combustion compliant with ISO 10694, where the organic carbon concentration was multiplied by 1.724. N<sub>min</sub> content was determined in 1 M KCl extraction in air-dry samples (ratio 1:5) using flow analysis (FIA) and spectrometric.

Soil characterization. The experiment was conducted on the Calcaric Luvisol (according to WRB, 2014). Soil texture was silt loam on loam and heavy clay loam. The pH<sub>KCl</sub> value in the 0–20 cm soil layer was within the optimal range for winter wheat, namely 5.9–6.4, humus – 1.91–2.33%, i.e., the values were low and average. The content of P<sub>2</sub>O<sub>5</sub> was 148–165 mg kg<sup>-1</sup>, which was average, and that of K<sub>2</sub>O was 200–216 mg kg<sup>-1</sup> – high.

In spring,  $N_{min}$  concentration was distributed across the soil layers as follows: at 0–30 cm – 9.4  $\pm$  1.58 mg kg<sup>-1</sup> in 2019 and 6.2  $\pm$  3.45 mg kg<sup>-1</sup> in 2020. At the 30–60 cm layer, it was 5.4  $\pm$  0.62 and 3.1  $\pm$  2.04 mg kg<sup>-1</sup>, respectively.  $N_{min}$  concentration converted to kg ha<sup>-1</sup> was obtained as follows: at the 0–30 cm layer, it was 42.5  $\pm$  7.09 kg ha<sup>-1</sup> and at the 30–60 cm layer – 24.2 $\pm$ 2.77 kg ha<sup>-1</sup> with the total level at 0–60 cm – 66.7  $\pm$  9.75 kg ha<sup>-1</sup> in 2019. In 2020,  $N_{min}$  content at those layers was 28.0  $\pm$  15.53, 14.0  $\pm$  9.16 and 42.0  $\pm$  24.69 kg ha<sup>-1</sup>, respectively. According to the assessment valid in Lithuania (Staugaitis, Vaišvila, 2019),  $N_{min}$  content in soil in spring was low in both years, but in 2020, it was still lower by a third compared to 2019.

Weather conditions. 2018–2019 season. September was dry and warm with a daily mean air temperature of 15°C and it was 2.2°C above the standard climate normal (SCN). 19.6 mm of precipitation fell during the month, i.e., it was 3.7 times lower than the SCN. Due to the drought, wheat germination was delayed. In October–November, the daily mean temperature values were  $1.4^{\circ}$ C and  $0.6^{\circ}$ C higher than the SCN, and the soil moisture was normal due to sufficient rainfall in October. The plants were well rooted in November, rich in green colour, and their height reached 7–10 cm. The winter in that region was warm and mild, the average daily temperature was  $0.03^{\circ}$ C in December,  $-4.1^{\circ}$ C in January,  $1.8^{\circ}$ C in February, and  $3.9^{\circ}$ C in March. The winter wheat overwintered well; plant growth resumed during the third 10-day period of March. The mean air temperature was  $8.4^{\circ}$ C in April and  $12.5^{\circ}$ C in May and those values were favourable for plant growth. The plants survived under drought conditions from April to the second 10-day period of May, depleting moisture reserves accumulated after the winter, however, during the last week the plants felt moisture scarcity and plant leaves appeared wilted in the daytime. By the end of April, the winter wheat was perfectly tillered and had already reached the beginning of stem elongation (BBCH 30).



Fig 1. Ten-day-mean air temperature (°C) during winter wheat growth (data of Kybartai Meteorological Station)

It rained profusely in the second half of May, and eventually the precipitation fell in the form of heavy rainfall. June was hot and not rainy. The mean daily temperature of that month was  $20.4^{\circ}$ C or  $4.8^{\circ}$ C higher than the SCN, and the precipitation was only 25.7 mm (SCN – 50 mm). During that period, the plants felt a lack of moisture again. During the first ten days of July, 60.6 mm of precipitation fell, and that was enough to restore moisture reserves in the soil. In the second and third 10-day periods, there was little rainfall, and the weather was warm which allowed normal grain ripening in ears.



Fig. 19. Ten-day rainfall (mm) during winter wheat growth season (data of Kybartai Meteorological Station)

2019-2020 season. It was 1–3°C warmer than usual in September–November 2019 and the monthly precipitation rate reached 44–47 mm, only in November the rainfall was lower – 13.2 mm. The sown winter wheat germinated evenly, and the plants were 8–12 cm tall by December. The moisture of the soil ploughing layer ranged from normal to dryish; however, at that time water evaporation was slow and moisture was sufficient for the plants. The winter was unusually warm: the mean daily temperature values in December–February were 2.8–2.9°C, and it was a little colder in March – 1.8°C. The winter wheat overwintered well, and its condition remained almost unchanged during the winter until the beginning of April, when its growth resumed. April and May were cool, however, the amount of precipitation varied significantly: only 2.1 mm in April and 93.8 mm in May. Dry March and almost rainless weather in April dried up the soil; therefore, the plants felt a lack of moisture and were less tillered in the second half of April. Rainy May restored soil moisture reserves, and an even

rainier June, when 129.4 mm of rain fell during the month, led to excess moisture in that month and facilitated the high spread of septoria leaf blotch (*zymoseptoria tritici*) and less of tan spot (*drechslera tritici-repentis*). July and the first 10-day period of August were cool, slightly humid and favourable to grain formation in ears.

### **RESULTS AND DISCUSSION**

Nitrate nitrogen levels in the soil in the 0–30 cm deep layer in BBCH stage 65 increased with increasing nitrogen fertilizer rates in both study years (Fig 3). However, the evenness and amounts of growth varied. 2019 nitrate nitrogen content ranged from 1.42 to 22.97 mg kg<sup>-1</sup> in the soil and increased steadily with increasing nitrogen fertilizer rates. 2020 the amount of nitrate nitrogen in this soil layer was 2.03 - 6.39 mg kg<sup>-1</sup> of soil. Fertilizers also increased the nitrogen content of this form, but the increase was not so uniform and when described by the regression equation, the coefficient of determination was obtained lower than in 2019.



Fig. 3. Influence of nitrogen fertilizers on nitrate nitrogen content in soil in 0-30 cm deep layer in winter wheat crop in BBCH stage 65

Investigating the amount of ammoniacal nitrogen in the 0-30 cm deep soil layer BBCH 65 in 2019 similar trends were obtained (Fig 4). Meanwhile, in 2020. Ammonia nitrogen content was very little affected by the increase of nitrogen fertilizer rates (coefficient of determination R2 - 0.3292)



Fig. 4. Influence of nitrogen fertilizers on ammonia nitrogen content in soil in 0-30 cm deep layer in winter wheat crop in BBCH stage 65

Nitrate nitrogen content in the deeper soil layer (30–60 cm) in the winter wheat crop in BBCH stage 65 was less affected by the increase in nitrogen fertilizer rates than in the topsoil (Fig 5).

In both years of the study, that effect was similar, with coefficients of determination of 0.6197 and 0.6609, respectively.



Fig. 5. Influence of nitrogen fertilizers on nitrate nitrogen content in soil in 30-60 cm deep layer in winter wheat crop in BBCH stage 65

Meanwhile, for ammonia nitrogen in the 30–60 cm soil layer, the increase of nitrogen fertilizer rates was very unequal in different study years (Fig. 6). 2019 a strong dependence of ammonia nitrogen on nitrogen fertilizer rates was determined (R2 - 0.8706). 2020 no such dependence was found (R2 - 0.0636).



Fig. 6. Influence of nitrogen fertilizers on ammonia nitrogen content in soil in 30-60 cm deep layer in winter wheat crop in BBCH stage 65

To determine how much unused nitrogen remained in the soil, we also examined the amounts of nitrate and ammoniacal nitrogen in the soil after peeling the wheat. The results of the studies differed again in individual research years. 0-30 cm depth in 2019. nitrate nitrogen content strongly correlated with fertilizer rates, the coefficient of determination was 0.9671 (Fig 7). Meanwhile, in 2020. this dependence was significantly weaker (R2 - 0.5275).



Fig. 7. Influence of nitrogen fertilizers on the amount of nitrate nitrogen in the soil in the layer of 0-30 cm depth in the winter wheat crop after harvest

The same trends were found when studying the amount of ammoniacal nitrogen in the 0-30 cm deep soil layer (Fig. 8).



Fig. 8. Influence of nitrogen fertilizers on the amount of ammoniacal nitrogen in the soil in the 0-30 cm layer in the winter wheat crop after harvest

Nitrate nitrogen levels in the soil depth of 30-60 cm with increasing nitrogen fertilizer rates in 2019 increased (Fig. 9). Although the increase was not uniform, it was positively correlated with the increase of fertilizer rates, the coefficient of determination was 0.6131. 2020 no correlation was found between the increase in nitrogen fertilizer rates and the amount of nitrate nitrogen in the soil. This may have been influenced by rainy, with heavy rains in late June-early July: unused nitrate nitrogen was leached from the soil.



Fig. 9. Influence of nitrogen fertilizers on the amount of nitrate nitrogen in the soil in the layer of 30-60 cm depth in the winter wheat crop after harvest

The relationship between the amount of ammoniacal nitrogen in the soil layer at a depth of 30-60 cm and the increase of nitrogen fertilizer rates in 2019. not identified (Fig. 10). 2020 ammonia nitrogen content after winter wheat harvest at a depth of 30-60 cm decreased with increasing fertilizer rates. Although the decrease was small, it strongly correlated with the increase of fertilizer rates (R2 - 0.8131).



Fig. 10. Influence of nitrogen fertilizers on ammonia nitrogen content in soil in a layer of 30-60 cm depth in winter wheat crop after harvest

2019 in all cases of the study, a strong linear relationship between nitrate nitrogen content in soil and nitrogen fertilizer content suggests that increasing fertilizer rates significantly increased leachable nitrogen, thus increasing the risk to the environment and human health (Sestak et al., 2014). 2020 this dependence was weaker, in some cases non-existent. This may have been influenced by different meteorological conditions during wheat vegetation. The strong influence of meteorological conditions on the movement of these nitrogen forms in soil has been pointed out by other authors (Kyllmar et al., 2006; Rutkowska, Fotyma, 2011). Nitrogen fertilisers improved the nutritional value and technological properties of grain during the experiment. This is pointed out by other researchers, arguing that higher nitrogen fertiliser rates are more important for both yield and product quality, and especially in this latitude, where there are fewer sunny days and the climate is maritime and continental (Juchnevičienė et al., 2016). Fertilising with N<sub>120</sub> rate, the agronomic efficiency of nitrogen fertilisers was higher and this is the focus of many researchers (Hawkesford, 2014; Tabak et al., 2020). However, when fertilising with N<sub>180</sub> and N<sub>240</sub> rates, a lot of unused nitrate nitrogen remained in the 0–60 cm soil layer after harvesting. This is a potential threat for nitrates to groundwater pollution when fertilised with such nitrogen rates (Sestak et al., 2014).

# CONCLUSIONS

1. The increase in fertilizer rates had the greatest impact on the nitrate nitrogen form, which is most prone to leaching and pollution. Nitrate nitrogen levels in the soil during the winter wheat flowering stage (BBCH 65) in both studies were directly correlated with the increase in nitrogen fertilizer rates (coefficients of determination ranged from 0.6197 to 0.9046).

2. Ammonia nitrogen content in soil in BBCH stage 65 in 2019 correlated with the increase of nitrogen fertilizer rates (R2 - 0.7708 and 0.8706). 2020 the relationship between these indicators was weak or non-existent.

3. Nitrate nitrogen levels in the soil after harvest were strongly correlated with the increase in fertilizer rates in 2019. In 2020 the amount of nitrate nitrogen in the soil may have decreased due to high precipitation, so the dependence between these indicators was weak or non-existent.

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# SCOTS PINE AND NORWAY SPRUCE STEM PARAMETERS IN SITES WITH DIFFERENT STAND DENSITIES IN LITHUANIA

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## **EXTENDED ABSTRACT**

## **RELEVANCE OF THE TOPIC**

Many internal (tree genetics) and external (natural - environmental factors, humaninduced - forest management) factors have an impact on the development of trees with good quality stemwood [1-4]. The stemwood quality is caused by several silvicultural parameters: stand density, stem radial increment, tree diameter at breast height (DBH), tree height increment, number and size of branches, and branch age [5-7].

Norway spruce (*Picea abies* (L.) H. Karst) covers 21.0% and Scots pine (*Pinus sylvestris* L.) – 34.6% of the forested area In Lithuania [8]. The assessment of stemwood quality of both Norway spruce and Scots pine is an important measure because these species cover the highest forested areas in Lithuania, also provide big economic benefit and profit from the forestry sector. Recently, the stemwood quality of these tree species has not been extensively studied [9-14], which may provide additional knowledge not only for forest science but also for practical forestry. This study aimed to determine the influence of stand density on stem branch parameters of Norway spruce and Scots pine trees.

## MATERIAL AND METHODS

Four sites of 36-43-years old Norway spruce and two sites of 31-38-years old Scots pine were selected in a long-term experimental area, established in 1990–1992 [21]. The study sites were distributed in different regions of Lithuania. Different sites were characterised by different stand densities (from minimum 500-600 to about 3-4 thousand trees ha<sup>-1</sup> or even 8 thousand tree ha<sup>-1</sup>) and thinning intensities (no thinning, and 1-4 times per stand age, in this case, during the 40-years period).

The measured parameters included tree height, diameter at breast height, height of the lowest live branch, height of the lowest dead branch, and the diameters of each branch (cm) along a butt log (hereafter, 0–6-meters log). The measurements were performed according to the standard methods, used in forest science and practical forestry. The calculations of all stem branch parameters were made for the whole 0–6-meters long log, and separately for different its sections (0–3-meters log and 3–6-meters log) if measure from the ground level.

## **RESULTS AND CONCLUSIONS**

The results of this study provided new knowledge about stem quality of relatively young pine and spruce trees, when they were grown under different conditions – stand densities and thinning regimes. The results showed that branch diameters along the stem 6-meters log decreased significantly with increasing stand density (Figure 1, where an example for Scots pine is given).



Figure 1. Mean values of branch diameter in 0-6-meter log ( $D_{br0-6}$ ) in two Scots pine study sites (201 and 206). Bars show Std Error of the mean. Different capital letter show statistically significant differences between the sites at p<0.05.

The correlation between branch diameter in 0-6-meters log and all estimated branch parameters was strong for both studied species. The parameters from the 3-6-meters log had strong correlation with the those from the 0-3-meters log. It showed that it is possible to estimate the branch parameters only in the lower stem section (up to 3 meters from the ground) to have relatively reliable result.

In this study, the best fitted models for prognosis of stem quality, were also developed, and they included stand density, tree diameter at breast height, and mean branch diameter or diameter of the thickest branch in 0–3-meters log.

Keywords: branch diameter, stand characteristics, coniferous species, models.

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# THE INFLUENCE OF CROP DIVERSIFICATION AND MANAGEMENT SYSTEMS ON SOIL SUSTAINABILITY AND PLANT PRODUCTIVITY

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#### ABSTRACT

Growing concern about environmental and climate problems are forcing the search for effective solutions for soil and crop management. One of the most important goals is to conserve and enhance soil quality and sustainability. Soil productivity is largely dependent on the quantity of organic matter that affects soil viability and crop productivity. Soil organic matter (SOM) is recognized as an indicator of soil quality, involves improving soil quality by increasing water and nutrient retention, which results in higher plant productivity. Soil organic matter affects the physical, chemical and biological properties of soil and crop productivity.

Crop and soil management decisions regarding crop rotation, tillage and fertilization are among the practices that can significantly affect soil productivity. Crop diversification is one of the most ecologically feasible, cost effective and rational ways to stabilize soil organic carbon stocks and help adapt to climate change. Crop diversification is a mean to develop cropping systems, which are more resilient and better adapted to the biotic and abiotic stresses associated with climate change. Functionally diverse crop rotations increased soil organic carbon concentrations. The effect of crop diversification on SOM depends on the plant root system and plant residues. Different rotations that include crops with different life cycles could lead to additional benefits of reducing the weed seed bank. Under moisture shortage conditions the crop diversification can also be a viable strategy to increase farm level crop productivity and plant nutrients availability. Contrasting tillage system influences soil physical attributes, such as structure, water holding capacity, rooting depth, the decomposition of SOM and the release of  $CO_2$  into the environment. The stabilization of humus levels and the improvement of carbon sequestration in soils can help stabilization of climate change and soil degradation.

Keywords: crop rotation, tillage system, soil, SOM, plant productivity

## LITERATURE REVIEW

The European Green Course and the National Progress Plan aim at climate change mitigation measures, climate-neutral agriculture and the economy. Addressing these challenges requires, in particular, halting soil degradation and improving soil quality and protecting biodiversity. The degree of soil degradation is determined by soil properties and soil-forming factors such as climate, land use, or soil management. Soil degradation processes are affected by some farming systems and practices that can help to better protect and conserve soil resources.

Soil is very important for the state of the ecosystem due to its many important functions: 1) providing food, fiber, and fuel; 2) decomposition of organic matter (soil organic matter plays a key role in maintaining basic soil functions); 3) recycling of essential nutrients; 4) detoxification of organic contaminants; 5) carbon sequestration; 6) regulation of water quality and supply; 7) habitat for soil organisms; 8) source of raw materials (clay, sand, gravel). The process of soil degradation, in which anthropogenic, physical and chemical effects alter soil properties and loses its basic, yield-determining properties, has a negative impact on the health of both humans and ecosystems [1].

Productive soils are the fundamental bases for agricultural sustainability and crop production. Due to this, right soil and crop management must be implemented and developed due to provide agricultural production and save our environment. Present world-wide concern is related to soil degradation problems, such as salinization, soil erosion by wind and water, acidification and, finally, soil contamination [2]. Growth of human being is also a great challenge due to feed them by food produced in a sustainable way. Practices need to be environmentally sound: increase carbon sequestration, prevent replenishment of plant nutrients from the soil [3].

One of the very important indicators of soil quality is organic carbon. Soil organic carbon (SOC) forms a large part of the global carbon cycle. Its amount depends on the intensity of photosynthesis and loss of respiration [4, 5]. Soil organic carbon regulates and improves many biological and physical (porosity, structure, infiltration rate) properties of soil, retains macronutrient cations (K, Ca, Mg) in forms accessible to plants [6, 7]. Nitrogen, phosphorus, sulfur, and trace elements are considered to be components of soil organic matter that are slowly released due to mineralization processes in the soil [6]. Soil organic carbon sustainability as a feature of the ecosystem [8] is based on a balance between the decomposition of microorganisms on the one hand and physical and chemical processes on the other [9] and, together with climate influence (temperature and humidity regimes) determine SOC turnover [10]. Decrease in SOC can lead to soil degradation, disrupt soil ability to retain water and nutrient supply to plants [11, 12, 13, 14, 15, 16]. Improved carbon sequestration in soil can help mitigate climate change, eliminate soil degradation, and improve food security [17]. The applied agro-measures can not only reduce or increase the amount of organic carbon and other nutrients in the soil, but also affect their stability [18, 19]. Soil organic matter is an important factor in maintaining the long-term productivity of ecosystems [20].

It is therefore necessary to improve plant production technologies that will help maintain soil fertility and increase soil viability. This would be crop diversification and the application of sustainable tillage systems.

Over the last few decades, crop rotation has been dramatically simplified to monoculture [21]. Long-term monoculture cropping systems decrease soil health under temperate conditions, independent of soil tillage, when compared to more complex extended crop rotations [22, 23]. Crop diversification is one of the easiest ways to reduce agricultural productivity instability, increase temporary and spatial biodiversity, and increase ecosystem capacity quickly to restore the initial productive state [24], helps to stabilize agricultural crop and weeds communities, i.e., changes the composition of the weed community, regulates their number. Changes in the sowing methods and terms of different crops with different growth cycles (winter, summer crops) and needs create unfavourable conditions and disrupt the life cycle of weeds [25]. It is important to make proper use of the ability of crop to tolerate and inhibit weeds [26, 27]. In conditions of moisture scarcity, crop diversification may also be an appropriate strategy to increase agricultural crop productivity (Mango et al., 2018). Multivariate and short crop rotation with cereals and oilseed rape and with cereals and sugar beet were the most studied [28, 29]. Legumes crops play an important role in crop rotation. They meet the need for nitrogen and restore soil fertility allowing a reduction in CO2 and N2O emissions compared to mineral nitrogen fertilizers [30]. Peas are a good pre-crop for other plants. They increase the diversity of soil microorganisms and their activity [31].

Many studies have been performed with legume crops on nitrogen fixation activity [32, 33], but their effect on the intensity of  $CO_2$  metabolism has been little studied. For winter wheat and oilseed rape grown under peas, the yield was obtained significantly higher than when grown after winter barley or wheat [34]. Weeds and diseases spread more abundantly in monoculture, pedofauna decreased, durability of soil aggregates decreased, soil drainage and aeration properties deteriorated [29, 35] studies.

Growing soil-restoring crops in monoculture or catch crops improves nutrient management [36], reduces nitrogen losses to the environment [37], and changes phytosanitary status [38]. Studies have shown that continuous cultivation of catch crops increased SOC by 2%, but also increased N-mineralization capacity by 25% [39]. In intensive farming systems, the incorporation of catch crop biomass into the soil increases soil microbiological activity, microbial respiration, release of various gas streams [40]. Such studies are lacking. The impact of catch crop insertion and transformation on soil properties and crop rotation productivity should be assessed.

Tillage affected water and plant nutrition regimes, which means that it influences most of the plant growth factors that determine yield and its quality [41]. Many researchers note the negative effects of mechanical soil degradation on the environment: water pollution, loss of SOM (soil organic matter), reduced soil water capacity, which reduces soil productivity and plant productivity [42, 43] and food material losses [44].

Plough tillage (PT) is common practice under moderate climatic conditions. The goal of ploughing is to burrow crop residues (straw), to loosen soil by improving soil physical properties. Ploughed soil is loose, warm, and ready to be tilled for crop sowing and its establishment. However, soil changes due to intensive tillage may bring some negative consequences: soil structure deterioration, plough pan formation, soil moisture reduction [45, 46]. The PT can also decrease aggregate stability in water, reduce total and air-filled porosity, soil sealing after intensive rain fall in the spring [47]. Due to plough pan occurrence, the PT application can decrease crop rooting ability, soil water percolation [48], result in biodiversity reduction [49, 50, 51]. It was determined, that ploughing increases biological decomposition of plant biomass. This is related to higher oxygen content in soil and faster OM decomposition rate in the plough-soil layer [51]. Intensive OM decomposition is the reason to increase carbon dioxide emission [52] and to decreases soil nutrients availability [53]. It should be noticed that in many cases, PT has positive effect to increase crop yielding ability, if crop rotations are managed [54, 55].

Through benefits to soil health, the continuous NT (no-till) systems, conducted under common conservation agriculture principles, can also mitigate the impacts of global climate change. The increases of OM content can help increase C sequestration, thus reducing net CO<sub>2</sub> emission and slowing global warming [56, 57]. Reduced tillage improved soil structure by increasing the number of sustainable aggregates [58, 59, 60], but agrochemical and physical properties deteriorated [61, 62]. According to other research data, minimization of tillage also degrades the physical properties of the soil - density, hardness, and air permeability [63, 64], but increases the number of earthworms and weeds [65]. By reducing the intensity of tillage, the moisture in the soil decreases [66], the water content in the soil increases [64]. The longterm research use of direct sowing has resulted in lower soil porosity, moisture and organic C content, and higher density than conventional tillage. When plants were sown directly into loose and non-loose soil, the physical properties deteriorated, but the moisture content in the 0-10cm layer increased [55], the soil was wetter [67, 68]. Higher soil moisture ensured faster and more even seed germination [69]. The abundance of segetal plant species and individuals is determined not only by the history of a particular field and the formation of a seed bank, but also by the applied agricultural systems and their intensity. Non-annual tillage inevitably leads to an increase in weeds, especially perennials [29, 65, 70]. Simplification of tillage substantially reduces plant productivity [70], while sometimes the method of tillage does not affect the yield [71]. Long-term (1994–2013) studies of zero and conventional tillage have shown that pea and bean yields were significantly higher by ploughing and winter wheat and barley compared to maize by no-till, but the differences between cultivations were small. Yields were more dependent on rainfall. Changes in wet and dry conditions are projected to increase annually in the future, i.e., spring conditions will be more diverse. In such a climate, the effect of zero

tillage on yield can be negative, positive, or neutral, and in the long run, zero tillage appears to have only a minor effect on plant adaptation to a changing climate [72].

According to long-term studies, the use of sustainable farming systems (including direct sowing) has increased soil organic carbon and improved soil physical properties, while intensive tillage has led to poorer soil properties with poorer structure, porosity and aeration The results of research on simplified tillage often differ significantly, and sometimes even contradict each other. This is influenced by the degree of soil cultivation, the use of chemical plant protection products, the intensity of fertilization and the biological properties of the crops grown. Therefore, the same agro-measure gives different results in different soils. Little research has been done on short crop rotations with bean crops under simplified tillage conditions. Short crop rotations have mostly been studied using traditional tillage. Until now, crop rotation research has mostly been limited to the assessment of soil agrophysical quality and crop yield, but little attention has been paid to  $CO_2$  flow rate in relation to SOC studies [72, 67].

We hypothesized that technological and biological measures (reduced tillage and crop rotation with peas and catch crop) will improve *Cambisol* properties due to resist anthropogenic degradation factors, to guide directions of soil CO<sub>2</sub> emission, to stabilize or increase SOM resources, to improve soil structure and aggregation in relation to maintain soil fertility and farming profitability.

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# COMPARATIVE RESEARCH OF THERMAL PROPERTIES OF COARSE ENERGY CROPS

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#### ABSTRACT

In Lithuania, as in the world, constantly being searched new crops, which would be suitable for energy conversion. Such crops must be unnecessary for the quality of the soil, applicable growing and post-harvest processing technologies. They must also be distinguished by high yields, while ensuring minimal impact on the environment. Much attention is paid to the coarse-energy crops group. It includes perennials and annuals crops. However, if we want to use biofuels of such coarse-energy crops for thermochemical conversion, it's important to know their thermal properties, i.e. their calorific value, ash content and ash melting temperature characteristics. Often efforts are made to use additional mineral fertilizers during cultivation, thus improving the yield of energy crops. In this case, it's necessary to assess whether the use of mineral fertilizers has a positive effect on the properties of energy crops, whether it is simply inappropriate to use an agrotechnical operation that requires additional energy costs, also increases by cost of fertilizers and fertilization.

The aim of the study is to determine the thermal properties of coarse-energy crops (perennials –  $Artemisia \ dubia$  Wall. and  $Miscanthus \times giganteus$ , annuals –  $Cannabis \ sativa$  L.) and to evaluate the expediency of using mineral nitrogen fertilization technology for perennial crops.

Coarse-energy crops were grown in a plantation set up at an experimental basis of Lithuanian Research Centre for Agriculture and Forestry, and the research work on fuel preparation and thermal conversion was carried out at the Laboratory of Biomass Processes, Logistics and Solid Fuel Processing of the Faculty of Agricultural Engineering, Vytautas Magnus University.

The average calorific value of *Cannabis* (17.92 $\pm$ 0.24 MJ kg<sup>-1</sup>) was found to be only 2.08 % and 3.66 % lower than that of *Miscanthus* and *Artemisia*, respectively. The calorific value of perennial crops can be increased by fertilizing them with mineral nitrogen, but only up to 1.51 % with maximum fertilization. The average ash content of *Cannabis* (3.36 $\pm$ 0.23 %) is 1.25 and 2.22 times higher than that of perennial crops (*Artemisia* and *Miscanthus*, respectively). Fertilization with mineral nitrogen has negative influence of the amount of crops ash. The lowest primary ash deformation (648 $\pm$ 8 °C) was recorded for *Cannabis*.

Fertilization with mineral nitrogen didn't affect the calorific value and ash content of crops, except for Artemisia. Fertilizing them with  $N_{170}$  – ash content is increased 1.3 times. The most significant influence on mineral nitrogen was found on the softening temperature characteristic of *Miscanthus* ash.

**Keywords:** Artemisia dubia Wall., Miscanthus×giganteus, Cannabis sativa L., coarse-energy crops, calorific value, ash content, ash melting temperature

# IMPORTANCE OF FORAGE LEGUMES TO THE AVAILABILITY OF SOIL MINERAL NITROGEN IN DIFFERENT SOIL TILLAGE SYSTEMS IN ORGANIC FARMING

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#### ABSTRACT

Including legumes in crop rotation as cover crops, relay intercrops or bi-crops, is a potential way of increasing the available N supply for cereals. In this perspective, legumes could play important role for sustainable environment and plant productivity. In three-years (2018-2020) experiment were compared rotations sequences: 1) oat (Avena sativa L.) - winter wheat (Triticum aestivum L.) - spring wheat (O-WW-SW); 2) forage legume- winter wheat - spring wheat (FL-WW-SW); 3) oat + forage legume (relay intercrop) - winter wheat + forage legume (bi-crop) - spring wheat (post-legume) (O+FL-WW+FL-SW). In rotations were cultivated forage legumes: black medic, BM (Medicago lupulina L.), white clover, WC (Trifolium repens L.), and Egyptian clover, EC (T. alexandrinum L.). For all of them, the first and second rotation for oat, forage legumes, winter wheat and spring wheat conventional tillage and sowing (CTS) were applied. In the first and third rotation and only for winter wheat were applied strip-tillage and sowing (STS). The soil samples were collected at 0-30 cm and 30-60 cm depths for the analysis of soil mineral nitrogen (SMN) content. The aim of study was to determine the effect of bicrops winter wheat-forage legume and STS on SMN variation in soil and cereal productivity compared to crop rotation without forage legume and with, using CTS. SMN content after forage legumes ploughing before pre-sowing winter wheat was significantly influenced by autumn tillage methods. The SMN content in the 0–30 cm layer of soil was significantly increased by CTS (1.7–2.1 times) compared to STS. Significant differences in the SMN were established when the growing season started in spring, were applied CTS (30-60 cm) and growing winter wheat after ploughing BM (61.4%) and WC (71.4%). The influence of WC and BM on the change in SMN remained in the third year of spring wheat cultivation compared to crop rotations without forage legumes. A strong significant positive correlation was found between SMN and winter wheat grain yield.

Keywords: legumes; cereals; nitrogen; strip-tillage; conventional tillage

### **INTRODUCTION**

Conservation agriculture more and more important internationally. It is aimed to make better use of agricultural resources through the integrated management of available soil, water and biological resources, combined with limited external inputs [1]. It contributes to environmental conservation and to sustainable agricultural production by maintaining a permanent or semi-permanent organic soil cover [2]. Conservation tillage, i.e. the use of tillage techniques which seek to reduce soil disturbance [3] and to maximize soil cover by crop species diversification [4], is an essential component of conservation agriculture. The optimisation of inputs and similar yields compared to conventional tillage, make conservation agriculture a profitable system compared to the tillage based agriculture [5].

Soil and crop management practices such as tillage, cover cropping and crop rotation can affect soil quality and soil health indicators, specifically the soil pH and organic matter levels [6]. Including legumes in crop rotation is a potential way of increasing the available N supply for cereals at low cost [7,8]. Various cropping strategies and management practices such as diversification of cropping systems by crop rotation, conservation tillage, and the use of cover crops have been promoted to enhance crop productivity and ecosystem services [9]

Over the last years, traditional agroecosystems have been progressively simplified and are now highly dependent on external inputs of energy andagrochemicals [10]. Conventional tillage (CT) is a controversial issue, fraught by a high variability over time and space [11]. In order to limit the environmental impact of agriculture, alternatives to traditional systems have been proposed [12]. Compared to classical plough tillage, reduced tillage has several advantages, such as reduction of fuel costs, decreased disturbance of soil organisms, preservation of soil fertility, higher soil macroporosity, better water retention [13,14,15]. However, reduced tillage also influences soil cover through a higher retention of crop residues at soil surface, compared to ploughing which incorporates residues in the soil. [12].

Another way to increase soil cover throughout the rotation is combining strip-tillage with forage legumes as living mulch between cash crops. Thus, ecology farming system is a new practice for crop production in the Lithuania. Growing cereals in a leguminous living mulch (bi-cropping) could reduce soil erosion, increase soil organic matter and in accumulation of large amounts of the nutrients [16,17,12]. It also have a potential for fixing nitrogen and can improve the availability of nitrogen for the next crop.

This research presents the crop yields of the rotations for the first three years of the experiment. The main objective of this study was therefore to investigate how rotational yields and soil mineral N are affected by the different forage legumes species and using different tillage system.

## **MATERIALS AND METHODS**

Field experiments were conducted at the Joniškėlis Experimental Station of the Lithuanian Research Centre for Agriculture and Forestry in the northern part of Central Lithuania's lowland. The soil of the experimental site is *Endocalcari Endohypogleyic Cambisol*, whose texture is clay loam on silty clay with deeper lying sandy loam. The soil (0–25 cm) is close to neutral (pH–6.1), medium in phosphorus (P<sub>2</sub>O<sub>5</sub> 146 mg kg<sup>-1</sup>), high in potassium (K<sub>2</sub>O 276 mg kg<sup>-1</sup>) and moderate in humus (2.54%).

#### Experimental site and crop management.

Field experiments were performed during 2018–2020 crops growing seasons. In the field experiment rotation sequences were compared: 1) oat (*Avena sativa* L., cv. 'Migla DS') – winter wheat (*Triticum aestivum* L., cv. 'Gaja DS') – spring wheat (O–WW–SW); 2) forage legume – winter wheat – spring wheat (FL–WW–SW); 3) oat + forage legume (relay intercrop) – winter wheat + forage legume (bi-crop) – spring wheat (post-legume) (O+FL–WW+FL–SW). Forage legume: black medic, BM (*Medicago lupulina* L., cv. 'Arka 133 DS'), white clover, WC (*Trifolium repens* L., cv. 'Nemuniai'), and Egyptian clover, EC (*T. alexandrinum* L., cv. 'Cleopatra') were cultivated in rotations. The first and second rotation for oat, forage legumes, winter wheat and spring wheat were applied conventional tillage and sowing (CTS). In the first and third rotation and only for winter wheat were applied strip-till and sowing (STS). The control treatments were winter wheat grown as monocrop (CTS) in cereal sequence (O–WW–SW). The experiment follows a two-factor field experiment in a randomized complete block design with two main treatments of soil tillage; conventional deep inversion tillage on one side, and strip-till treatments on the other side. The field trial was laid out in a randomized with three replicates and the size of each plot was  $20.0 \times 6.0$  m.

## **Experimental setup**

In 2018, year of the experiment establishment, was used for monocrops and relay intercropping systems. The oat was sown on 23 April 2018 at a seeding rate of 450 seeds  $m^{-2}$ 

using a drill at a 3 cm depth. The forage legume species were intercropped in oats on April 2018 at a seed rate of 50 seeds m<sup>-2</sup>. The forage legume seeds were sown at a 2 cm depth using a drill. At the beginning of August, all underground biomass of forage legumes was chopped and spread. The winter wheat (cv. 'Gaja'); was seeded at the middle of September. Tillage was then applied according to the respective treatments. In the conventional tillage, the following were used: deep inversion tillage (ploughed 23–25 cm depth), a pre-sowing cultivation unit and a seed drill. A seed drill sowed seeds to a depth of 2.5–3.0 cm at a row spacing of 0.125 m. The winter wheat was sown at a seeding rate of 450 seeds m<sup>-2</sup>. In the strip-till system, a one-pass tillage, winter wheat sowing operations were performed using a Pro Till 3T hybrid machine manufactured by Mzuri, Great Britain. The row spacing was 0.33 m and the sowing depth was also 2.5–3.0 cm and was sown at a seeding rate of 380 seeds m<sup>-2</sup>. In August 2019, after the harvest of a winter wheat (straw was chopped and spread by harvesting machine), each plot was ploughed 23–25 cm depth. Spring wheat (cv. 'Granaria') was seeded in spring on April 2020, with the seed drill, at the 2.5–3.0 cm depth, and at a seeding rate of 450 seeds m<sup>-2</sup>. Crops were cultivated according to organic management practices.

#### Plant and soil analyses

The oat, winter wheat and spring wheat grains were harvested, when the majority of plants had reached the BBCH 87 stage. The grain yield was measured by weighing and converting to standard moisture (14%). The total energy (GJ ha<sup>-1</sup>) content in the cereals yield of crop sequences was calculated as follows:

TE (=[ $(Y_0 \times 19.08)/1000 + (Y_{ww} \times 18.56)/1000 + (Y_{sw} \times 18.56)/1000]$ ,

where  $Y_0$  is the grain yield of oat (kg ha<sup>-1</sup> DM);  $Y_{ww}$  is the grain yield of winter wheat (kg ha<sup>-1</sup> DM); and  $Y_{sw}$  is the grain yield of spring wheat (kg ha<sup>-1</sup> DM); 19.08 and 18.56 are the total energy (MJ kg<sup>-1</sup> DM) content accumulated in grain yield of oat and wheat respectively.

The soil samples for the analyses of soil mineral nitrogen (SMN) were collected each year at 0–30 cm and 30–60 cm depths. The SMN was measured 4 times during the experimental period: after winter wheat sowing in autumn 21-11-2018 (assessment 1); in spring before the winter wheat vegetation renewed 25-03-2019 (assessment 2); in autumn, when all plot of experimental were ploughed 16-10-2019 (assessment 3); and before spring wheat sowing in spring 23-04-2020 (assessment 4). ). Soil mineral nitrogen content (SMN = N–NO<sub>3</sub> + NH<sub>4</sub>) was measured N–NO<sub>3</sub> by ionometric and NH<sub>4</sub> by spectrophotometric methods. Samples for SMN analyses – in 1mol L<sup>-1</sup> KCl extract, w/v ratio 1:5.

### Weather conditions

The meteorological data were collected at the stationary meteorological station "iMetos" at Joniškėlis Experimental Station, LAMMC, Lithuania. The seasonal rainfall varied during the experimental period (Fig. 1). In 2018, meteorological conditions were characterised by the wet November and very dry December. The winter period from December 2018 to February 2019 was mild and dry. In spring 2019, the weather was warmer and drier than usual. It was very dry in April. During summer period, June had the warmest and least precipitation. July month received the most rainfall during the all season. The autumn was warmer and the amount of precipitation was enough for soil. The winter period in 2019 was warmer and the monthly distribution of precipitation was significantly more even than 2018. The spring of 2020 was warm and early, but there was not much rainfall accumulation. In general, the meteorology of

2018–2020 seasons was favourable for nitrogen preservation in the soil because dry periods prevailed in this years.

# Statistical analysis

Statistical analysis was performed using software from the statistical data processing package *SELEKCIJA* [18]. The research data were processed by the one-factor analysis of variance as well as correlation (ANOVA version 3.1 software and STAT\_ENG version 1.5). The differences in research data between the treatment were means for significant effects were separated using Duncan's multiple range tests at the 5% probability level ( $p \le 0.05$ ).

# **RESULTS AND DISCUSSIONS**

## SMN in rotations and tillage

SMN content after forage legums ploughing before pre-sowing winter wheat was significantly influenced by autumn tillage methods (Fig. 1). The SMN content in the 0–30 cm layer of soil was significantly increased by CTS (1.7–2.1 times) compared to STS. Strip-tillage did not have a significant effect on SMN changes. After ploughed legumes (CTS), there was a strong increase of SMN in the topsoil, in rotations with BM–WW and WC–WW. In strip-tillage, the higher increase of SMN was established in rotation O+EC–WW+EC.



Fig. 1. Treatment effects on concentrations of soil mineral nitrate, measured in autumn 2018 after to sowing winter wheat (assessment 1).

Note. Monocrops: O–WW – oat–winter wheat, BM–WW – black medick– winter wheat, WC–WW – white clover– winter wheat, EC–WW – Egyptian clover–winter wheat; bi-crops: O+BM–WW+BM – oat+black medick–winter wheat+black medick, O+WC–WW+WC – oat+white clover–winter wheat+white clover, O+EC–WW+EC – oat+Egyptian clover–winter wheat+Egyptian clover; means with different letters within the experiment differ according to Duncan's multiple test ( $p \le 0.01$ )

Significant differences in the SMN were establish when the growing season started in spring, were applied CTS (30–60 cm) and growing winter wheat after ploughing BM (61.4%) and WC (71.4%) (Fig. 2). Significantly different changes in SMN established (0-30 cm) were observed in rotation BM–WW, compared with control (monocrop rotation). Comparing autumn

(assessment 1) and spring (assessment 2) nitrogen content in the soil, study showed that the nitrogen content, in the spring, in rotations with forage legumes decreased 50–65 % 0-30 cm) and increase 52–55 % (30-60 cm) and where CTS was applied. Soil N content was minimum ranging between autumn and spring period in the STS.



Fig. 2. Treatment effects on concentrations of soil mineral nitrate, measured in spring 2019 before winter wheat vegetation renewed (assessment 2).

Note. Monocrops: O–WW – oat–winter wheat, BM–WW – black medick– winter wheat, WC–WW – white clover– winter wheat, EC–WW – Egyptian clover–winter wheat; bi-crops: O+BM–WW+BM – oat+black medick–winter wheat+black medick, O+WC–WW+WC – oat+white clover–winter wheat+white clover, O+EC–WW+EC – oat+Egyptian clover–winter wheat+Egyptian clover; means with different letters within the experiment differ according to Duncan's multiple test ( $p \le 0.01$ )

After winter wheat harvesting in 2019, the highest SMN the highest values were observed in the rotation of BM–WW (0–30 cm) and O–BM+WW–BM (30–60 cm) (Fig. 3). The similar available soil N content values were established in both tillage systems. The values of the soil layer show differences depending on forage legumes. The lower values were observed in the cereal monoculture (CTS).



Fig. 3. Treatment effects on concentrations of soil mineral nitrate, measured in autumn 2019 when all plot of experimental were ploughed (assessment 3).

Note. Monocrops: O–WW – oat–winter wheat, BM–WW – black medick– winter wheat, WC–WW – white clover– winter wheat, EC–WW – Egyptian clover–winter wheat; bi-crops: O+BM–WW+BM – oat+black medick–winter wheat+black medick, O+WC–WW+WC – oat+white clover–winter wheat+white clover, O+EC–WW+EC – oat+Egyptian clover–winter wheat+Egyptian clover; means with different letters within the experiment differ according to Duncan's multiple test ( $p \le 0.01$ )

Our results is in agreement with author who show that the soil available N in the top 20 cm prior to sowing wheat do not corresponds to the net inputs of fixed N or the amount of residual N from legume crops or green manure remaining at the end of the growing season [8]. The analysis performed in spring period, demonstrates the greater amount of SMN results compared assessment 3 (Fig. 4). The influence of WC and BM on the change in SMN remained in the third year of spring wheat cultivation compared to crop rotations without forage legumes. The highest value was following EC (CTS). There was a strong increase in soil N in all over assessment time in the STS. Our study also showed, that at the end of the growing season for a legume crop, the aboveground residues and the organic matter below the surface (roots and nodules) are the reservoirs for mineralization. Several studies report that N associated with nodules and roots can represent between 30% and 60% of total N accumulated by legumes [19,20].



Fig. 4. Treatment effects on concentrations of soil mineral nitrate, measured in spring 2020 before spring wheat sowing (assessment 4).

Note. Monocrops: O–WW – oat–winter wheat, BM–WW – black medick– winter wheat, WC–WW – white clover– winter wheat, EC–WW – Egyptian clover–winter wheat; bi-crops: O+BM–WW+BM – oat+black medick–winter wheat+black medick, O+WC–WW+WC – oat+white clover–winter wheat+white clover, O+EC–WW+EC – oat+Egyptian clover–winter wheat+Egyptian clover; means with different letters within the experiment differ according to Duncan's multiple test ( $p \le 0.01$ )

At the end of the growing season for a legume crop, the aboveground residues and the organic matter below the surface (roots and nodules) are the reservoirs for mineralization [6]. In our study, legumes increased N content in the soil. Other studies suggest that legume N plays a key role in contributing to the soil and may be the source of between 30-75% of the total mineral N accumulating after legumes [5.21]. The N mineralization rezults showed different results depending on the forage legumes species. The effect of tillage treatment was less marked.

### Grain cereal yields in rotations and tillage

Assessing the productivity of different rotations according to the accumulated total energy in the grain cereal, it was found that significantly lower (21.2–27.8%) total energy was accumulated in the rotations with forage legumes monocultures compared to the cereal rotations CTS (Fig. 5).



Fig. 5. The amount of total energy accumulated in grain cereal yield of different rotation sequences in 2018 – 2020.

Note. Monocrops: O – oat, BM – black medick, WC – white clover, EC – Egyptian clover, WW – winter wheat, SW – spring wheat; relay intercrops: O+BM – oat–black medick, O+WC – oat–white clover, O+EC – oat–Egyptian clover; bi-crops: WW+BM – winter wheat–black medick, WW+WC – winter wheat–white clover, WW+EC – – winter wheat–Egyptian clover; CTS – conventional tillage, STS – strip-tillage; means followed by the same letters are not significantly different at  $p \le 0.01$ .

The use of legume in the rotation shows a clear benefit in terms of soil N reservoir and its use by the cereal crop in the following season [6]. Most of the total energy was accumulated in the crop rotation with bi-crop WW+WC (STS) at the grain harvest. There the total energy content was 16.5–19.7% higher compared to the cereal rotation using conventional (CTS) and 18.9–22.2% higher using STS. In bi-crop rotation WW+WC, the total energy accumulated was significantly higher than in bi-crop rotation WW+BM. However, the rotation WW+WC was not significantly different from the crop rotation EC – insertion as "dead" mulch (STS). The bi-crop WW+EC in terms of total energy accumulation an intermediate position between the crop rotation with WW+BM and bi-crop WW+WC.

Winter wheat yields changed, depending on soil mineral content in the soil. A strong significant positive correlation was found between winter wheat grain yield and MNS in the 0-60 cm layer. (Fig. 6).



Fig. 6. Dependence of winter wheat grain yield on the amount of mineral nitrogen accumulated in the soil (0–60 cm) during autumn (assessment 1) and spring (assessment 2).

## CONCLUSIONS

This experiment has shown that forage legumes play a crucial role in agriculture systems. The use of forage legume crops in the rotation show a strong benefit in terms of soil N reservoir and its use by the cereal crop in the following season. Forage legume developing a sufficient amount of SMN before the seeding of the main crop. The highest SMN uptake by the rotations in the four assessment sites occurred after to sowing winter wheat (CTS) and before spring wheat sowing (STS). There was a close relationship between the SMN and by winter wheat yield during the growing season. The winter wheat and spring wheat in total energy with STS was more efficient than CTS. The best combination appeared to be O+WC–WW+WCbi–SW cultivation in the STS.

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# HEIGHT AND CHLOROPLAST PIGMENTS RESPONSE IN POPULUS HYBRIDS UNDER THE IMPACT OF DIFFERENT ENVIRONMENTAL CONDITIONS DURING ROOTING

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#### ABSTRACT

To meet the needs of carbon sequestration and production of raw materials from renewable natural resources for the bioenergy and timber market of the European Union, it is necessary to expand forest plantation areas. The efficiency of short-rotation forestry depends primarily on the selection of hybrids and clones, suitable for the local environmental conditions. We postulate that ecogenetic response, ecogenetic plasticity, and genotypic variation of hybrid poplars (*Populus* L.) grown in field trial depend on the peculiarities of hybrids and clones, as well as on environmental conditions at rooting and growing in the greenhouse and on genetic pre-adaptations to native environmental conditions of their geographical origin. The study aimed to estimate growth and biochemical response, the ecogenetic plasticity, genotypic variation of adaptive traits, and epigenetically regulated adaptability of clones of *Populus* hybrids predisposed by the simulated environmental conditions at their rooting time. The research was performed with the 12 cultivars and experimental clones of one intraspecific cross of poplars and four different interspecific hybrids of poplars. The results indicated that there are different responses of hybrid clones to rooting conditions, which later have an impact on growth rhythm and biochemical traits when grown under natural conditions, as well as on their different genetic parameters.

Keywords: populus, hybrids, clones, ecogenetic response, genetic variation

### **INTRODUCTION**

The importance of forests as a source of renewable energy and raw materials and CO<sub>2</sub> absorber from the atmosphere, thus reducing greenhouse gases and climate change is increasingly emphasized in the world, leading to the expansion of forest areas in many countries, and especially - short-rotation forest (SRF) plantations. Poplar hybrids are very fastgrowing, their wood is valuable for the paper the industry and bioenergy, it is a promising tree species both economically and ecologically and is important for the development of intensive SRF plantation in Lithuania. Climate change is a growing threat to the sustainability of existing as well as newly planted forests and poses new challenges to forestry science and forestry. Due to rising temperatures, CO<sub>2</sub> concentrations, and increasing precipitation in northern Europe, many deciduous tree species are expected to improve their growth rate, but climate change is also a negative factor in forest ecosystems, such as increased frost, heat and frost, droughts, mild winters, reduced snow cover and depth of the frozen ground, etc. It directly or indirectly causes stress to trees, disturbs their growth rhythm, development, growth or even damages them, disturbs physiological processes, and induces changes in the biochemical response. Epigenetic phenomena often occur here - adaptive changes due to changes in environmental conditions or stressors that resulted from changes in gene expression [13,6,4]. Current developments are much faster than those undergoing severe climate change in the post-glacial period. Such severe stress can cause not only seasonal and physiological changes in species, but through increased natural selection, the genotype of the offspring may be altered and genetic diversity reduced. Short-term adaptation can be achieved through physiological, phenotypic, and morphological plasticity, but long-term genetic adaptation to large environmental changes

and even species evolution can only be ensured by genetic variation and selection. One of the biggest challenges facing forest breeding and growing is that change in tree characteristics and adaptation capacity is difficult to predict under climate change. The significance of epigenetics in tree adaptation has been studied for some time [3,10,15]. Epigenetic processes are known to determine heritable alterations in gene function but do not alter the primary DNA sequence [2]. Earlier environment impact affects the ability of a tree to respond to its the current environment, determines its survival or the manifestation of certain properties or attributes. It is known that epigenetic changes occurring in natural populations may correlate with naturally occurring phenotypic variation [4], but this natural variation in epigenetic markers and their relationship to phenotypic traits is still not well studied. Detailed studies and research on the epigenetics of forest trees and their results would make it much easier to predict the success of their adaptation to the climatic conditions of a particular area [4]. There is no doubt that epigenetics should be considered as one of the important components in modern forest tree breeding and biotechnology. The ability of long-lived plants to adapt to environmental conditions in the context of global warming is crucial to both the conservation of species and ecosystems and the improvement of their certain properties. The aim of the study was to estimate growth and biochemical response, the ecogenetic plasticity, genotypic variation, and heritability of adaptive traits, and epigenetically regulated adaptability of clones of Populus hybrids grown in field trials predisposed by simulated environmental conditions at their rooting and growing time.

## **MATERIAL & METHODS**

## Material

The research was performed with 12cultivars and experimental clones of one intraspecific cross of poplars (*P. trichocarpa* Torr. & Gray.) and four different interspecific hybrids of poplars (*P. deltoides* L.  $\times$  *P. nigra*, *P. deltoides*  $\times$  *P. trichocarpa*, *P. maximowiczii* A. Henry  $\times$  *P. trichocarpa*, and *P. balsamifera* L.  $\times$  *P. trichocarpa*). Aspen (*P. temula* L.) was used as control. The study used clones with distinguished bio-ecological characteristics from the LAMMC Institute of Forestry collection of hybrid poplars. The clonal test plantation was planted using vegetatively propagated plants rooted and grown under contrasting environmental conditions simulated in the Phytotron of LAMMC Institute of Forestry. The clonal experimental plantation was established in Jonava's forest district of the State Forest Enterprise.

#### Methods

Ramets of hybrid poplar clones for the testing in clonal field trial were rooted in Phytotron greenhouse under different environment conditions (treatments). Cuttings of each clone were planted into the squared plastic pots  $(15 \times 15 \times 20 \text{ cm})$  filled with 3.5 l of peat soil (Klasmann KTS-1) and placed on irrigation tables. One-third of ramets were rooted outdoors under natural conditions, one-third in the Phytotron greenhouse, and one-third in Phytotron greenhouse with additional heating of pots with substrate from below. During the rooting of cuttings, the average air temperature in the greenhouse was 25 °C, in outdoors it was 19 °C. The average soil temperature outdoors was 19 °C, in the greenhouse – 22 °C, in pots with additional heating – 24 °C. Air humidity was kept between 65 and 85% using an automated fog sprinkle system. The plants were regularly watered by temporary (0.5 hours a day) flooding pots on irrigation tables to fully saturate the soil and keep soil moisture at 80–95% of the full moisture capacity (FMC) throughout the experiment. In the middle of the greenhouse were moved to grow outdoors, half of the ramets that were rooted outdoors were moved to the greenhouse, and heating of roots was turned off and they continued to grow in the greenhouse. The rest of them were moved
outdoors. These resulted in six combinations of treatments: cool rooting and cool growing conditions (CR+CG), cool rooting and warm growing conditions (CR+WG), warm rooting and cool growing conditions (WR+CG), warm rooting and warm growing conditions (WR+WG), hot rooting and cool growing conditions (HR+CG), hot rooting and warm growing conditions (HR+WG). Aspen was planted as a control tree to the field.

Next spring the trees were outplanted in a clonal field trial in Jonava's forest district. Tree height was measured twice - at the beginning of the growing season and the end. For biochemical analysis, the third leaf from the top of the leading shoot was sampled from 5 trees in each clone at the end of August. The photosynthetic pigments were extracted from 0.05 g of fresh leaf/needle material in 3 ml of N,N'-dimethylformamide (DMF). The light absorption was measured at 480, 664, 647 nm wavelengths. Chlorophyll a/b ratios and concentrations of chlorophylls a and b and carotenoids were calculated according to Wellburn [22]. All spectrophotometrical measurements were made using spectrophotometer SPECORD 210 Plus (Germany). All data are expressed on a leaf fresh weight basis,  $\mu g g^{-1}$  FW. To estimate the significance of the effects of various factors - treatments (rooting conditions and growing conditions)), blocks, clones, and hybrids and their interaction with treatments, the multifactor variance analysis was performed on single-tree data using the MIXED procedure (procedure option – "Covparms") of the SAS software [20] which is based on mixed model equations (MME) and the restricted maximum likelihood (REML) method. The following linear models were used for the joint analyses (1) of the treatments and the separate analyses (2) of individual treatment:

$$y_{ijklm} = \mu + tr_j + tg_k + tr_j tg_k + c_i + c_i tr_j + c_i tg_k + b_m + e_{ijklm},$$
(1)

$$w_{im} = \mu + c_i + b_m + e_{im}, \qquad (2)$$

where  $y_{ijklm}$  is an observation on the  $l^{th}$  ramet from the  $i^{th}$  clone in the  $m^{th}$  block in the  $j^{th}$  rooting and  $k^{th}$  groving treatment,  $y_{ilm}$  is an observation on the  $i^{th}$  ramet from the  $i^{th}$  clone in the  $m^{th}$ block,  $\mu$  is the overall mean,  $tr_j$  is the fixed effect due to the  $j^{th}$  rooting treatment,  $tg_k$  is the fixed effect due to the  $k^{th}$  growing treatment  $b_m$  is the fixed effect due to the  $m^{th}$  block,  $c_i$  is the random effect due to the  $i^{th}$  clone,  $c_i tr_j$  is the random effect of interaction between the  $i^{th}$  clone and  $k^{th}$ growing treatment,  $c_i tg_k$  is the random effect of interaction between the  $i^{th}$  clone and  $k^{th}$ growing treatment,  $\varepsilon_{ijklm}$  and  $\varepsilon_{iklm}$  are the random residuals. The model assumes that the random effects are normally distributed with the expectation of zero and corresponding variances:  $\sigma_c^2$ ,

 $\sigma_{c*tr}^2$ ,  $\sigma_{c*tg}^2$ ,  $\sigma_{c*tg}^2$  and  $\sigma_e^2$ . Assumptions of normal distribution of residuals and variance homogeneity were tested using the GLM and UNIVARIATE procedures of the SAS software [20]. Statistical significance of the effects of fixed factors – treatments, blocks, and interactions between treatments and blocks was estimated by *P*-test (Tests3 option) using the MIXED procedure of the SAS software [20]. *Z* tests were carried out to determine where random effects were significantly different from zero. Least-squares mean estimates were obtained for treatments, as well as for hybrids and clones in each treatment. Statistical significance (at *P* < 0.05) of differences between least-squares means was tested using *t*-test (the PDIFF option under the LSMEAN statement of the MIXED procedure of the SAS software [20]. Using statistical model 2 clonal variance components were estimated:

$$VC_c^2 = \sigma_c^2 / (\sigma_c^2 + \sigma_e^2), \tag{3}$$

where:  $VC_c^2$  is the clonal variance component,  $\sigma_c^2$  is the clonal variance,  $\sigma_e^2$  is random residual. The variance component of each effect was expressed as a percentage of dispersion of all analysed (included in the model) random effects. The means of treatments, blocks, hybrids, and clones by blocks and treatments as well as their standard errors were determined using the

MEANS procedure of the SAS software [20]. Genetic parameters were estimated using variance analysis results separately for each treatment. Clonal heritability coefficient on the level of individuals for each trait was calculated by the following formula:

$$H_m^2 = \sigma_c^2 / \sigma_{phen}^2 , \qquad (4)$$

where:  $H_i^2$  is the coefficient of clonal individual heritability,  $\sigma_i^2$  is the clonal variance,  $\sigma_{phen}^2$  is the phenotypic variance. The standard errors of heritability coefficient under an unequal number of trees per family were calculated based on Becker [1]. Clonal heritability coefficient (repeatability) on the level of means was estimated using the formula:

$$H_m^2 = \sigma_c^2 / (\sigma_c^2 + (\sigma_e^2 / k)) , \qquad (5)$$

where:  $H_m^2$  is the clonal heritability coefficient on the level of means,  $\sigma_c^2$  is the clonal variance,  $\sigma_e^2$  is the random variance, *k* is the coefficient showing the mean number of trees per clone. The errors of heritability coefficients were estimated according to Swiger et al [21] method modified by Becker [1] for an uneven number of observations. Genotypic variation coefficient in every clonal trial was estimated based on Falconer [8], Falconer et al [9]. The genotypic gain (genetic improvement effect) was estimated according to Nanson [17].

#### **RESULTS AND DISCUSSIONS**

# Dependence of hybrid *Populus* growing rate in a clonal field trial on the rooting-growing conditions

The highest mean tree height was obtained under CR+CG and WR+CG conditions, accordingly 139 and 137 cm and lowest under WR+WG conditions - 117 cm (Fig.1). The highest hybrid among all was P. deltoides  $\times$  P. trichocarpa. Mean height reached among all conditions reached 128 cm which exceeds the average height of the aspen (as a control tree). The best growth conditions for *P. deltoides* × *P. trichocarpa* hybrid were CR+CG (Fig.1). Large height differences obtained for P. deltoides  $\times$  P. nigra. Under CR+CG conditions height was 179 cm, however under WR+WG conditions more than 1 m less – only 77 cm. P. deltoides  $\times$ P. nigra is a hybrid of southern origin. Although P. deltoides naturally grows in moist habitats, it also requires higher air temperatures, which were higher in the greenhouse than under natural weather conditions in the field plots [5]. *P.nigra* habitat in Europe does not extend far north, which indicates that cold is a limiting factor [7], therefore, the higher temperature prevailing in the greenhouse led to better growth of *P. deltoides* × *P. nigra*. Hybrids responded differently to heat on their roots during the rooting time. Under HR+WG conditions 3 of 5 hybrids grew weaker than under HR+CG. P. trichocarpa  $\times$  P. trichocarpa under HR+CG demonstrated the lowest mean height among all environments which may indicate the stress experienced by the hybrid. Plants can transduce positive and negative signals among roots and shoots to coordinate growth rate and behavior, and adapt to variable environments. When environmental stresses suppress root growth and change root distribution, shoot growth and functions may also be reduced as an effect of root-to-shoot signaling [18]. Interestingly, P. balsamifera  $\times$  P. trichocarpa under HR+CG demonstrated the highest mean height among all environments (Fig.1). This hybrid is characterized by a high plasticity level, it shows that trees can respond to and adapt to climate and environmental change in a relatively short time [11].



Fig. 1. Mean height (cm) in *Populus* hybrid under different rooting-growing conditions (for abbreviations see Materials & Methods). Hybrid type abbreviations: B×T – *P. balsamifera* × *P. trichocarpa*, D×N –P. *deltoides* × *P. nigra*, D×T – *P. deltoides* × *P. trichocarpa*, M×T – P. *maximowiczii* ×*P. trichocarpa*, T×T – P. *trichocarpa* × *P. trichocarpa*, D×D – P. *tremula* 

# Dependence of pigment content in leaves of *Populus* in clonal field trial on different factors

### Impact of hybrids and treatments in Phytotron greenhouse on pigment content in hybrid Populus leaves in clonal field trial

Analysis of variance showed that the effect of plant growing conditions in Phytotron greenhouse on the amount of all the pigments and the chlorophyll ratio in trees outplanted in field trial was highly significant (P < 0.001) (Table 1). The impact of rooting conditions of cuttings in the greenhouse was highly significant (P < 0.001) on chlorophyll A, carotenoids, and chlorophyll ratio of outplanted trees, but not on chlorophyll B (P = 0.0195) (Table 1). The impact of interaction rooting × growing conditions was also very significant on chlorophyll A, chlorophyll ratio, and carotenoids. This interaction did not affect chlorophyll B content (P = 0.0715) (Table 1). The dependence of the amount of photosynthetic pigments on environmental conditions was also found in Pliūra et al. [19] studies.

The highest mean chlorophyll A quantity (1.49  $\mu$ g g<sup>-1</sup> FW) was obtained for *P. deltoides* × *P. nigra* hybrid. Hybrid D×N had the highest chlorophyll A content under CR+WG and WR+CG conditions (Fig. 2). Though *P. trichocarpa* × *P. trichocarpa* hybrid had the lowest mean chlorophyll A quantity (1.25  $\mu$ g g<sup>-1</sup> FW), but under WR+WG conditions it reached 2.06  $\mu$ g g<sup>-1</sup> FW. Under changing environmental (rooting-growing) conditions *P. deltoides* × *P. trichocarpa* hybrid retained a fairly constant amount of chlorophyll A.

The most sensitive to environmental conditions was *P. deltoides*  $\times$  *P. nigra* hybrid. Changing levels of chlorophyll A due to stressors negatively affect the process of photosynthesis, which is directly related to plant growth. In our previous studies, this hybrid suffered significant growth losses due to environmental stressors under controlled environmental conditions [11].

Table 1. Results of multivariate ANOVA: *F*-criteria and significance of fixed effects of rooting and growing conditions and their interaction on different traits of *Populus* hybrids in the clonal field trial.

Effect	Num.DF	Den.DF	F value	Prob F	$P^*$	
Chlorophyll A						
Growing conditions	1	824	35.20	<.0001	***	
Rooting conditions	2	824	30.61	<.0001	***	
Interaction rooting $\times$ growing conditions	2	824	10.91	<.0001	***	
	Chlorophyll	В				
Growing conditions	1	824	14.84	0.0001	***	
Rooting conditions	2	824	3.96	0.0195	*	
Interaction rooting $\times$ growing conditions	2	824	2.65	0.0715		
Chlo	rophyll A and	d B ratio				
Growing conditions	1	824	24.01	<.0001	***	
Rooting conditions	2	824	21.65	<.0001	***	
Interaction rooting $\times$ growing conditions	2	824	7.48	0.0006	***	
Carotenoids						
Growing conditions	1	824	21.63	<.0001	***	
Rooting conditions	2	824	26.14	<.0001	***	
Interaction rooting $\times$ growing conditions	2	824	8.66	0.0002	***	
* Level of significance of affects is denoted by: $*0.01 < D < 0.05$ ; $***D < 0.001$						

\* Level of significance of effects is denoted by: \*0.01 < P < 0.05; \*\*\*P < 0.001

Under HR+CG and HR+WG conditions (when roots were heated during the rooting period) there were no significant differences between the hybrids according to chlorophyll A quantity. The amount of chlorophyll A in aspen used as a control species reached 1.5  $\mu$ g g<sup>-1</sup> FW. The maximum amount of chlorophyll A fixed under WR+WG conditions (Fig. 2).





The highest chlorophyll B amount was found under HR+WG conditions in *P. balsamifera*  $\times$  *P. trichocarpa* – 1.14 µg g<sup>-1</sup> FW and under CR+WG and WR+WG conditions in *P. deltoides*  $\times$  *P. nigra*, accordingly 1.13 and 1.11 µg g<sup>-1</sup> FW. The maximum value of chlorophyll B was obtained under WG conditions. The chlorophyll B amount of aspen reached 1.03 µg g<sup>-1</sup> FW. Carotenoids act to protect photosynthetic organisms, including chlorophylls, from the harmful effects of excessive exposure to light [12]. The amount of carotenoids usually is 1.5-2 times

less than the amount of chlorophyll. In our studies, carotenoid levels were also lower than that of chlorophyll (Fig. 2). The maximum value of carotenoids among all hybrids obtained under CR+WG conditions (Fig. 2). Besides, the amount of carotenoid was similar in all hybrids, ranging from 0.37 to 0.9  $\mu$ g g<sup>-1</sup> FW, regardless of the environment. The highest carotenoid content was obtained in the *P. deltoides* × *P. nigra* and *P. deltoides* × *P. trichocarpa* hybrids, which in its natural range is accustomed to absorbing more sunlight from the environment. Increased carotenoids improves adaptation to existing conditions because they expand the wavelength range of light that can drive photosynthesis [12]. Under changing environmental (rooting-growing) conditions carotenoid amount mostly varied in *P. trichocarpa* × *P. trichocarpa* – from 0.38 to 0.9 µg g<sup>-1</sup> FW. Environmental conditions had little effect on carotenoid quantity in *P. deltoides* × *P. trichocarpa* hybrid. The carotenoid content of aspen reached 0.61 µg g<sup>-1</sup> FW.

The maximum concentration of chlorophyll A and B ratio were obtained under CR+WG conditions. *P. deltoides*  $\times$  *P. trichocarpa* characterized by the highest chlorophyll A and B ratio, while *P. maximowiczii*  $\times$  *P. trichocarpa* – the lowest. The highest chlorophyll A and B ratio was found under CR+WG conditions in *P. balsamifera*  $\times$  *P. trichocarpa* – 2.18 and under WR+WG conditions in *P. trichocarpa*  $\times$  *P. trichocarpa* – 2.06. Plants respond to changing environmental conditions by changes in the composition of pigments in the chloroplasts. For proper functioning of the photosynthetic mechanism, the chlorophyll A/B ratio may decrease in leaves because chlorophyll A tends to degrade faster in stressful conditions than chlorophyll B [16].

# Changes of genetic parameters of different traits of trees in clonal field trial depending on rooting-growing treatments in Phytotron greenhouse

The clonal component of variation, which shows the share of clonal variation in the overall variability of traits, ranged from 27.85 to 65.90% for different traits under different treatments (rooting-growing conditions) (Table 2). The highest clonal variation component – 65.90% - was obtained for chlorophyll B under WR+WG conditions. The amount of pigments in most cases under CR+WG conditions was characterized by a higher clonal variation component than under other conditions. Clonal variation component of chlorophyll A decreased the most: from 64.57% under CR+WG conditions down to 27.85% under (0.01 < P < 0.05). Clonal variation component of chlorophyll A and B ratio under WR+CG conditions was only 3.66%, however, it was insignificant.

The highest heritability coefficient was obtained for chlorophyll B under CR+WG conditions ( $H_i^2 = 0.66$ ) and the lowest – for chlorophyll A and B ratio under WR+CG treatment ( $H_i^2 = 0.04$ ) and chlorophyll A under HR+WG treatment ( $H_i^2 = 0.28$ ). In CR+WG and WR+WG conditions, where the growing condition was outside the greenhouse, more than 60% of this variability was due to genotypic reasons (Table 2). High mean values of heritability coefficient indicate strong genotypic control of the trait. The decrease of values of heritability coefficients shows that in stressful environmental conditions ecological variation of these traits is greater concerning genotypic variation. High heritability coefficients indicate that the traits are strongly controlled genetically and less by random factors. The higher the coefficient of heritability the more the trait is valued from viewpoint of tree breeding, as it allows more precise identification of a genotype by its phenotype. Along with changes in environmental conditions (different treatments), the values of the heritability coefficient alter as well.

Trait	Treatment	Traits mean±se	Clonal variance component, ±se	<i>P</i> *	Clonal variance component, % ±se
	CR+CG	1.29±0.04	0.12±0.07	•	52.23±31.99
	CR+WG	$1.64 \pm 0.05$	0.38±0.18	*	64.57±31.53
Chloro-	WR+CG	$1.26 \pm 0.04$	$0.10 \pm 0.05$	*	$40.08 \pm 20.78$
phyll A	WR+WG	$1.58 \pm 0.05$	0.23±0.12	*	62.89±32.68
	HR+CG	$1.25 \pm 0.03$	$0.16\pm0.07$	*	60.28±29.65
	HR+WG	$1.09 \pm 0.03$	$0.05 \pm 0.03$		27.85±17.47
	CR+CG	$0.82 \pm 0.01$	$0.00 \pm 0.00$		30.00±20.02
	CR+WG	$0.89 \pm 0.02$	$0.05 \pm 0.02$	*	65.90±32.11
Chloro-	WR+CG	$0.81 \pm 0.02$	$0.03 \pm 0.01$	*	49.82±25.07
phyll B	WR+WG	$0.95 \pm 0.03$	$0.08 \pm 0.04$	*	61.10±31.85
	HR+CG	$0.83 \pm 0.01$	$0.02 \pm 0.01$	*	41.44±21.37
	HR+WG	$0.81 \pm 0.04$	$0.11 \pm 0.06$	*	48.86±27.94
	CR+CG	$0.54 \pm 0.01$	$0.00 \pm 0.00$		39.58±25.19
	CR+WG	$0.63 \pm 0.01$	$0.03 \pm 0.01$	*	$62.80 \pm 30.78$
Carote-	WR+CG	$0.55 \pm 0.01$	$0.03 \pm 0.01$	*	53.38±26.63
noids	WR+WG	$0.65 \pm 0.01$	$0.03 \pm 0.01$	*	64.24±33.31
	HR+CG	$0.53 \pm 0.01$	$0.01 \pm 0.00$	*	40.74±21.06
	HR+WG	$0.47 \pm 0.01$	$0.00 \pm 0.00$	*	33.68±20.37
	CR+CG	$1.56 \pm 0.03$	$0.05 \pm 0.03$		34.82±22.62
Chloro-	CR+WG	$1.81 \pm 0.03$	$0.11 \pm 0.05$	*	51.86±25.96
phyll A	WR+CG	$1.56\pm0.02$	$0.00 \pm 00.00$		$3.66 \pm 4.81$
and B	WR+WG	$1.70\pm0.03$	$0.04 \pm 0.02$	*	31.03±17.82
ratio	HR+CG	$1.51 \pm 0.02$	$0.05 \pm 0.02$	*	41.36±21.24
	HR+WG	$1.45 \pm 0.03$	$0.06 \pm 0.04$	*	35.31±21.19

Table 2. Genetic parameters of different traits of *Populus* hybrids in clonal field trial affected by different rooting-growing treatments: trait means, clonal variance component.

\*Level of significance of effects is denoted by: \*0.01<P<0.05

The lowest genotypic variation was found for chlorophyll A and B ratio (in WR+CG conditions) -3.74% (Table 3). The highest genotypic variation was found for chlorophyll B under HR+WG conditions -CVg reached 41.11%, however, it decreased more than 3 times under 15 conditions -12.12%. Differences in genotypic variation in different environmental conditions are determined by an uneven biochemical processes disruption rate of different clones and their different phenotypic plasticity. The highest value of the genetic benefit for each pigment was obtained under different environmental conditions. The value of the predicted genetic gain of chlorophyll B varies the most under different conditions. The highest predicted genetic gain was obtained for chlorophyll B (dG = 53.37%) under HR+WG treatment, however, under CR+CG treatment it was 18.75% (Table 3). The lowest genetic gain was obtained for chlorophyll A and B ratio (dG = 7.09%) under 25 treatment.

Table 3. Genetic parameters of different traits of *Populus* hybrids in field trial affected by different rooting-growing treatments: coefficient of genotypic variation ( $CV_G$ ), coefficient of individual heritability ( $H_i^2$ ), clonal mean heritability ( $H_m^2$ ), coefficient of phenotypic variation ( $CV_F$ ), and expected genetic gain (dG, dGm).

Trait	Treatment	$CV_{G},$	$H_{i^2} \pm $ s.e,	$H_{m^2} \pm s.e$	$CV_{F},$	dG, %	dGm,
		<u>%</u>	0.52+0.16	0.04+0.02	% 26.16	10 00	<u>%</u>
Chlorophyll A	CR+CG	27.10	$0.52\pm0.10$	$0.94 \pm 0.03$	30.10	10.00	54.08 42.12
	CR+WG	37.70	$0.05\pm0.11$	$0.97 \pm 0.02$	44.57	28.78	45.12
	WR+CG	26.22	$0.40\pm0.13$	$0.91\pm0.04$	40.64	16.29	36.95
1 2	WR+WG	30.72	$0.63 \pm 0.13$	0.96±0.02	37.44	23.55	36.02
	HR+CG	32.05	$0.60\pm0.12$	$0.96 \pm 0.02$	39.28	23.68	37.76
	HR+WG	20.97	$0.28 \pm 0.13$	$0.85 \pm 0.07$	39.08	10.88	33.32
	CR+CG	12.12	$0.30 \pm 0.14$	$0.87 \pm 0.07$	21.67	6.50	18.75
	CR+WG	25.97	$0.66 \pm 0.11$	$0.97 \pm 0.01$	30.36	20.01	29.43
Chlorophyll D	WR+CG	23.07	$0.50 \pm 0.13$	$0.94 \pm 0.02$	31.91	15.90	29.90
Споторнун в	WR+WG	30.51	0.61±0.13	$0.96 \pm 0.02$	37.76	23.07	36.22
	HR+CG	20.37	0.41±0.13	$0.92 \pm 0.04$	30.50	12.64	28.07
	HR+WG	41.11	$0.49 \pm 0.15$	$0.93 \pm 0.03$	57.09	27.90	53.37
	CR+CG	16.50	0.40±0.16	0.91±0.05	25.51	10.10	23.16
	CR+WG	30.51	0.63±0.12	$0.97 \pm 0.02$	36.55	22.95	35.27
	WR+CG	32.13	0.53±0.12	$0.94 \pm 0.03$	42.86	22.88	40.51
Carotenoids	WR+WG	27.59	0.64±0.13	$0.96 \pm 0.02$	33.25	21.36	32.06
	HR+CG	19.93	0.41±0.13	$0.92 \pm 0.04$	30.15	12.28	27.69
	HR+WG	18.24	$0.34 \pm 0.14$	$0.88 \pm 0.06$	30.80	10.37	27.22
Chlorophyll A and B ratio	CR+CG	14.97	0.35±0.15	$0.89 \pm 0.06$	24.76	8.62	22.01
	CR+WG	18.67	$0.52 \pm 0.13$	$0.95 \pm 0.02$	24.74	12.83	23.41
	WR+CG	3.74	$0.04 \pm 0.05$	0.36±0.13	19.54	0.71	7.09
	WR+WG	12.38	0.31±0.13	$0.87 \pm 0.06$	21.86	6.78	19.04
	HR+CG	15.70	0.41±0.13	$0.92 \pm 0.04$	23.88	9.88	21.98
	HR+WG	17.77	0.35±0.14	$0.89 \pm 0.05$	29.27	10.34	26.09

## 4. CONCLUSIONS

In our studies epigenetic phenomena were identified – tree indicators and genetic parameters depend on the conditions of the rooting-growing period. ANOVA has shown that the effect of plant rooting-growing conditions in phytotron on all the pigments content and the chlorophyll ratio in trees outplanted in field trial was highly significant. The greatest mean height of outplanted trees resulted from WR+CG rooting-growing conditions. *P. deltoides* × *P. trichocarpa* characterized by greatest mean height among all hybrids. The maximum amount of chlorophyll A resulted from WR+WG conditions, of chlorophyll B – from HR+WG. The highest predicted genetic gain was obtained for chlorophyll B – under CR+WG treatment, and the greatest heritability coefficient was obtained for chlorophyll B – under CR+WG treatment.

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## THE PHOTOPHYSIOLOGICAL ASPECTS FOR HIGHER NUTRITIONAL VALUE AND IMPROVED POST-HARVEST QUALITY OF LEAFY GREENS

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#### ABSTRACT

In recent years, the interest in a healthy diet and fresh-looking and nutritious vegetables increased. Leafy greens are one of the most consumed vegetables worldwide rich with health-promoting fiber, vitamins, polyphenols, and minerals, and protect against chronic and non-infectious metabolic disorders. Leafy vegetables can be produced under controlled environmental conditions, where the air temperature, humidity, CO<sub>2</sub> concentration, lighting are maintained. The recent decade of research confirmed that single or mixed light-emitting diode (LED) wavebands have direct promotional effects for the biosynthesis of secondary metabolites known as antioxidants in horticultural crops. However, there are only a few studies that investigated the quality preservation of vegetables during postharvest storage. The production of high-quality leafy greens raised new scientific ideas about post-harvest preservation through LEDs. This study aims to perform scientific research to evaluate the possibility to use LED radiation for quality preservation of leafy greens during post-harvest storage. Previously published studies demonstrated the influence of LED light on the enhanced or delayed loss of phytochemicals during post-harvest storage. For example, UV-A radiation increased the contents of polyphenols in watercress; red light led to the higher ascorbic acid content and inhibited yellowing and the degradation of chlorophyll, and decreased weight loss in broccoli; white, blue, green and red light improved the total chlorophyll, phenols vitamin C contents in cabbage. The secondary metabolites like organic acids are related to the undesirable enzymatic browning or yellowing of fresh-cut greens. Also, blue and red LEDs facilitate moisture loss by stimulating stomatal conductance and transpiration during storage, thereby improving aesthetic quality and acceptability to consumers. In this study, the effects of pre-harvest LED lighting conditions on the overall quality of leafy greens during postharvest storage will be reviewed.

Keywords: vegetables, lighting, storage.

#### **INTRODUCTION**

Nowadays, the demand for nutritious and fresh-looking vegetables is growing. Leafy greens are one of the most consumed vegetables worldwide, rich with health-promoting biologically active compounds like fiber, vitamin A, C, and E, polyphenols, and mineral nutrients, which may protect against human health chronic and non-infectious diseases [1]. Because of the higher levels of phytochemical compounds, young leafy vegetables like microgreens or baby-leaf greens are considered "functional food" [3]. This term came of interest in the possibility that selected foods might promote human health and modify one or more physiologic processes. Public interest in functional food is increasing because of higher health care costs [4].

The pre-harvest growing conditions during cultivation, and post-harvest conditions during the storage, impact the chemical composition and appealing appearance of the leafy vegetables [3]. Leafy greens can be produced in semi- or fully closed growing systems, where the air temperature, humidity,  $CO_2$  concentration, lighting, etc., can be controlled. However, light is the most important abiotic factor in controlled environments, which has a significant role in influencing physiological changes and secondary metabolite production in plants [3].

This study aims to review the pre and post-harvest LED light effects on vegetable quality preservation during the shelf-life.

In a few past decades, an increased number of studies have shown the beneficial effects of LED light on plant growth and quality [8]. LED light has been shown to enhance antioxidant and nutritional properties, sensory quality, and shelf-life in harvested vegetables [9]. Different outcomes can be achieved by changing the light spectrum, intensity and duration [8]. The plants can sense light through plant photomorphogenetic receptors phytochromes (PHYA to PHYE), cryptochromes (CRY1 to CRY3), phototropin (PHOT1 and PHOT2), and one UV-B resistance locus 8 (UVR8) [2]. Phytochromes are dimeric chromopeptides, with two forms: Pr (red lightabsorbing PHY) and Pfr (far-red light-absorbing PHY). The two forms of phytochromes are photoconvertible. Pr is synthesized when red (R) light (peak = 660 nm) is absorbed and is converted to Pfr when far-red (FR) light (peak = 730 nm) is absorbed. Pfr is considered to be a physiologically active form of phytochromes. Both forms of phytochromes have a common chromophore - linear tetrapyrrole. In some species, Pfr form of phytochromes A can be backtransformed to Pr form by a reaction that does not require light. A serine-threonine kinase is activated by PHYA and signal transduction is believed to involve cyclic guanosine monophosphate (cGMP), G-proteins, and calcium [10]. In plants, phytochromes are responsible for physiological responses of the plant and synthesis of some phytochemicals, like phenolic compounds (PC) [2]. Other receptors are cryptochromes. They are the receptors of blue (B) ultraviolet-A (UV-A) light radiation. CRY1 is a protein that binds both flavin and a pterin chromophore. By increasing irradiances of B light, the levels of CRY2 can be reduced, but it does not affect CRY1. Cryptochromes are known to mediate light-dependent redox reactions [10], regulate stomatal opening, biomass production, and biosynthesis of anthocyanins and carotenoids and chlorophylls [2]. Phototropins are flavoproteins, that are known to take part in phototropic responses to the direction of B light, green (G), or UV-A light. Phototropins can phosphorylate their serine and threonine residues [10]. These receptors are known to modulate stem elongation in response to ultraviolet B (UV-B) radiation before cryptochrome activation and mediate phototropic responses [2]. UV-B does not affect photosynthesis but it can be a threat to the integrity of plants. To adapt to the harmful effects of UV-B plants use the UV RESISTANCE LOCUS8 (UVR8) photoreceptor. This photoreceptor can make significant changes in gene expression that can lead to morphological adaptations and the production of flavonols that act as UV-B protectants. UVR8 photoreceptors take part in stomatal movement, phototropic bending, and entraining of the circadian clock. This receptor receives light using a triad of closely packed tryptophan residues and does not use chromophore. Before absorbing light, an inactive form of UVR8 is present as a homodimer. After absorbing UV-B light inactive homodimer is converted to an active monomer [11].

# EFFECTS OF PRE-HARVEST LED LIGHTING ON QUALITY OF LEAFY GREENS DURING POST-HARVEST STORAGE

The light factor has a significant effect on physiological changes and the production of metabolites in plants [3]. Previously published studies have shown the effect of LED light on the increased or delayed post-harvest loss of phytochemicals. Experiment with pak choi (*Brassica campestris* L. ssp. *chinensis* var. *communis*) showed that using UV-B lighting at the pre-harvest stage can influence levels of total flavonoids when plants were exposed to UV-B for ten days before harvest [13].

It was observed that using LED lighting at the pre-harvest stage may help to maintain vegetable quality for longer. Experiments with Chinese kale (*B. oleracea* var. *alboglabra* Bailey cv. DSCH) sprouts, when it was exposed to red light for 24 hours before harvest, showed that it could notably postpone the degradation of aliphatic, indole, and total glucosinolates

during post-harvest storage. Chinese kale sprouts were exposed to R light for 24 h before harvest. Measurements were taken on the first, second, and third day after harvest. Results showed that vitamin C level was remarkably higher in R light-treated sprouts on the first and second day after harvest compared with the control plants grown under white (W) light. Also, R light treatment enhanced total phenolic content (TPC) and maintained a higher level of antioxidant activity than the control plants treated only with W light [12].

Another experiment was performed with lettuce (*Lactuca sativa*) 'Lollo Bionda' when plants were exposed to the R LED lighting for five days before harvest. Results showed that using R light statistically significant decrease in nitrogen content was obtained. The same researchers published experiments with wild rocket (*Diplotaxis tenuifolia*). Plants were exposed to R, B, and FR lighting for three days before harvest. Results showed that under R light nitrogen content was significantly lower than in other groups [14]. Also, it was observed that under these conditions, vitamin C content was altered. The highest content of vitamin C was found in samples taken from plants grown under R and B light. Also, it was observed that plants grown under FR light had the shortest shelf-life [14].

# EFFECTS OF POST-HARVEST LED LIGHTING ON QUALITY OF LEAFY GREENS DURING POST-HARVEST STORAGE

LED lighting can be used to maintain the quality of vegetables during post-harvest storage. Previously published studies demonstrated the influence of LED light on the enhanced or delayed loss of phytochemicals during the post-harvest storage - UV-A (380-315 nm) light increased the contents of polyphenols in watercress [5]; R light (625-700 nm) led to the higher ascorbic acid content and inhibited yellowing and the degradation of chlorophyll, and decreased weight loss in broccoli [6]; white (W), B (425–490 nm), G (490–550 nm) and red light improved the total chlorophyll, phenols vitamin C contents in cabbage [5]. Besides, the secondary metabolites like organic acids are related to the undesirable enzymatic browning or yellowing of fresh-cut greens. Also, blue and red LEDs facilitate moisture loss by stimulating stomatal conductance and transpiration during the storage, thereby improving aesthetic quality and acceptability to consumers [7].

Kanazawa K. et al. [23] conducted an experiment where harvested spinach (Spinacia oleracea L.), radish (*Raphanus sativum* L.), parsley (*Petroselinum crispum* Mill.), Indian spinach (*Basella rubra* L.) were stored at 10 °C under UV-A (380–320 nm) and UV– B (280–320 nm) for three days, then stored for another six days. Samples for flavonoid content determination were taken daily. Control plants were stored in the darkness at the same temperature. Results showed that spinach irradiated with UV-B light had increased flavonoids during six days of storage, compared to those plants in the dark and under UV-A. Mature leaves of parsley and Indian spinach, and radish sprouts kept under UV-A and UV-B light, had significantly higher contents of kaempferol glycoside than control plants during six days of storage [23].

The concept of hormesis states that adding agent that can induce chemical or physical stress [18]. Such agents can be ultraviolet C (UV-C) radiation, which induced antioxidant activity. Recently, sub-lethal doses of UV-C have been assayed as a possible strategy in post-harvest technology. An experiment was conducted where broccoli heads were irradiated with different doses of UV-C (4, 7, 10, or 14 kJ m<sup>-2</sup>) and then stored at 20 °C for five days to accelerate senescence. According to results, chlorophyll degradation with 10 and 14 kJ m<sup>-2</sup> doses caused the most significant response. Total chlorophyll content during storage at 20 °C and chlorophyll degradation rate were slowed by the UV-C. After four days at 20°C, UV-C treated florets had approximately 53% more chlorophyll than control florets, which were stored in the darkness. The levels of chlorophyll a and b decreased during storage at 20°C and the UV-C treatments

delayed chlorophylls' degradation. After the treatment, broccoli had a higher antioxidant capacity than those stored in darkness. TPC increased under UV-C. During storage at 20 °C, TPC increased in broccoli regardless of the radiation treatment. However, the increment was higher in those of untreated broccoli. Florets treated with UV-C after 4 and 6 displayed lower levels of TPC [18].

Another experiment with fresh-cut vegetable leaves of red chard (Beta vulgaris) and rocket (Diplotaxis tenuifolia) was performed. The purpose of this study was to observe physiological and quality changes during storage depending on the used different spectral components of monochromatic light-emitting diode (LED). Leaves were stored under different lighting conditions (R, G, yellow (Y), W, B, and FR light) at 5 °C for ten days. Samples were taken on the first day, after 7 and 10 days. It was observed that all red chard under R, G, Y, W, and B light had increased contents of carotenoids after seven days of storage, except for FR compared to those stored in the dark. After ten days of storage, leaves under G and B light maintained higher carotenoid content. In rocket leaves, carotenoid content decrease after ten days was only associated with B light. Results show that no difference was found between the effects of lighting in red chard leaves after seven days of storage. Leaves under all lighting treatments had lower chlorophyll concentration than in samples that were stored in darkness. Only leaves treated with W light had a higher chlorophyll concentration at the end of the storage experiment compared with those kept in the dark. Interestingly, rocket leaves under R, G, Y, and B for seven days showed higher chlorophyll content compared to control. After ten days of storage, leaves treated with Y and W light had significantly higher contents of chlorophylls than in those leaves kept in the dark.

Light during storage resulted in statistically significant increases of antioxidant compounds in both red chard and rocket leaves. In both species, DPPH (2,2-diphenyl-1-picrylhydrazyl) increased under R and B light at seven days of storage, while at the 10<sup>th</sup>-day antioxidant capacity increased under all lighting treatments in red chard, and under R, G, Y, and B light in a rocket. TPC was increased under R, Y, W, and B light in both plant species after seven days of storage. After ten days, all light treatments had a significant impact on TPC increase in both red chard and rocket, compared to the control group, stored in the dark [19].

The experiment, performed by Aili Jiang et al. [15], showed that using R LED lightinduced a series of physiological and molecular responses that extended post-harvest quality and prolonged the shelf-life of commercially produced broccoli (*B. oleracea* var. *italica*, cv. 'You-xiu'). The results indicated that R LED light maintained the sensory appearance of broccoli, delayed yellowing and the degradation of chlorophyll, and decreased weight loss during the five days of storage at 20 °C under continuous R light, compared to control plants kept in the dark at the same temperature [15]. Similar to these findings in the experiment conducted by Gang Ma et al. [22], R light has shown the ability to delay yellowing and decrease ethylene production of broccoli. In contrast, B light did not affect [22]. Also, R light decreased the content of malondialdehyde (MDA). The activity of the antioxidant enzymes, peroxidase (POD), catalase (CAT), and ascorbate peroxidase (APX) was enhanced in LED-treated broccoli, while the expression of the chlorophyll degrading genes, chlorophyllase II (*BoCLH2*), chlorophyllase III (*BoCLH3*), and pheophorbide an oxygenase (*BoPAO*) was suppressed in the early stages of storage.

In contrast, no effect on chlorophyllase I (*BoCLH1*) was observed [15]. However, another experiment that was performed with broccoli sprouts showed that when used R and FR for stored sprouts decreased contents of TPC after four days of storage and even lower after 15 days, compared to sprouts stored in darkness. Furthermore, TPC was the lowest in plants treated with B light at 4, 8, 15 days and R light treated plants at 8 and 15 days [16]. Peng Jin et al. [17] investigated the effect of G LED light on broccoli heads during post-harvest storage. Vegetables were stored at  $25 \pm 1$  C for two days. Results showed that plants treated with G LED light had

a longer shelf-life than those under fluorescent light (400-700 nm) and plants stored in the dark. The shelf-life of broccoli florets treated with LED G light extended to almost three times that of control florets. During the storage, it was observed that chlorophyll content decreased in both control and treated broccoli florets. However, the chlorophyll degradation rate was significantly lower in G light-treated broccoli florets than in control florets. G light treatment significantly increased the content of TPC during storage time and was shown to significantly increase DPPH free radical scavenging activity in broccoli [17].

In an experiment conducted by Martina Loi et al. [20], fresh broccoli heads (*Brassica oleracea* L. var. *italica*) were harvested and stored for 20 days at 4 °C with continuous light of B, G, Y, R, and W light. Control plants were stored at the same temperature in the dark. Samples were taken after 5, 10, 15, and 20 days. Results showed that all plants stored under light treatments had significantly higher water loss than those stored in the dark. The highest water loss was determined in plants stored under Y and R lights. However, the TPC in plants under the same treatments increased up to 2.5-folds after 5 days of storage and maintained a significantly higher until the end of the storage time compared to the control plants [20].

In another study, brussels sprouts (*Brassica oleracea* var. *gemnifera*) were harvested and stored under continuous W, and B light at 22 °C, and control plants were placed under the same temperature. The biochemical analysis was done after 1, 5, and 10 days. The results showed that using W and B light yellowing was delayed, the green colour of outer and inner leaves was maintained. The study also showed that the outer leaves of the sprouts exposed to the above-LED lighting had higher contents of flavonoids and higher antioxidant activity than those sprouts stored in the dark [21].

In the Costa L. et al. [24] experiment, basil (*Ocimum basilicum* L.) leaves were stored at 20°C in the dark under low intensity (30–37 mol m<sup>-2</sup> s<sup>-1</sup>) R and FR light each day for 2 hours. Chlorophyll and ammonium (NH<sub>4</sub><sup>+</sup>) content were measured after harvest and after five days. Results showed that while R light pulses caused almost complete inhibition of chlorophyll degradation, 13% of the initial chlorophyll content was lost after five days of storage in FR light-treated leaves. The NH<sub>4</sub><sup>+</sup> content increased 2.5-fold during senescence in darkness, whereas in leaves treated with R light there was no ammonium accumulation after five days of storage. Compared to plants under R light and those stored in the dark, FR light did not reduce ammonium accumulation [24].

#### CONCLUSION

Various studies demonstrated that pre- and post-harvest LED lighting could be beneficial for altering metabolite contents in leafy greens during storage. However, there is still a lack of information regarding the most beneficial light spectral conditions and photon flux density for the maximum shelf-life and best overall quality of plants of different genotypes and maturity stages. Therefore, there is a need to develop an economically effective, safe, and nontoxic effective method to improve the storage quality of harvested vegetables.

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## CARBON AND NITROGEN CHANGES IN MINERAL TOPSOIL OF SCOTS PINE PLANTATIONS GROWING ON CLEAR-CUTTING

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#### ABSTRACT

Scots pine (*Pinus sylvestris* L.) is a dominant tree species in the Baltic region's hemiboreal forests and occupy 34.5% of all forested area in Lithuania. Typically, Scots pine (*Pinus sylvestris* L.) stands grow on nutrient-poor soils. The final clear-cutting in Lithuanian commercial forests, when mature stands are felled during one operation, is a traditional activity. The local forestry practice shows that clear-cutting disturbs the balance of forest functions for a certain period. When all logging residues are extracted from forest sites, phytocenoses with forest-based species composition, biodiversity and cover, and soil carbon and nutrient balance are disturbed in the ecosystem. Sustainable forestry follows the principle that harvesting practices should avoid negative influence on soil carbon and nitrogen, as key elements in the forest ecosystem. When assessing the fresh clear-cutting changes, it is also rational to assess how quickly newly established forest plantations return to the mature forest ecosystem's former nutrient levels.

Organic carbon and nitrogen concentrations in mineral topsoil of Scots pine (*Pinus sylvestris* L.) plantations on *Arenosols* were studied in Lithuania in 2020. The studied sites included fresh clearcutting and 8-, 30- and 101-years old Scots pine stands. The main study results showed that total and mineral nitrogen concentrations varied between the clear-cutting sites of different age and topsoil depths. However, the concentrations of organic carbon changed insignificantly after clear-cuttings.

Keywords: mineral soil, soil organic C concentration, soil N concentration, mature forest

## **INTRODUCTION**

In Lithuania, the National Forest Sector Development Program for 2012–2020 emphasizes the comprehensive benefits of forests for the economy and society. One of the four goals of forestry development in Lithuania is to maintain forest ecosystems' sustainability, taking into account their ecological and social role and the impact of climate change. Among other ecological functions of the forest, these ecosystems accumulate carbon dioxide and store carbon in soil and plant biomass, thereby reducing greenhouse gases in the atmosphere [1,2].

Final clear-cutting in Lithuanian commercial forests, when mature stands are felled during one operation, is a traditional activity. Despite that, it is evident that clear-cutting disturbs the balance of forest functions for a certain period. When all logging residues are extracted from the site, the final clear-cutting disturbs ecosystem carbon and nutrient balance. The recent studies show that various changes occur in the ecosystem after clear-cutting, and these changes continue for some time until the phytocenoses of the newly formed forest reach the site-specific species composition, biodiversity and cover. It is equally important to assess the changes in soil chemistry [2-6].

In order to clarify the processes that occur in the former forest sites after clear-cutting, both short-term and long-term studies are performed to monitor nutrient changes and the risk of leaching of mobile compounds to groundwater [3–9]. In terms of the recent climate change, the assessment of greenhouse gas emissions and organic carbon stocks in forests and logging sites has also received particular attention [2, 10,11].

It is well known that soil is one of the most important carbon and nitrogen pools, including approximately 75% of organic carbon and 95% nitrogen [12]. Carbon accumulation in forest ecosystems occurs mainly through forest vegetation, forest litter and soil [13,14]. The plant communities, biodiversity and cover in the site cause the carbon cycle and interaction between soil organic carbon (SOC) and N [15]. However, accurate estimates of carbon and nitrogen dynamics in the soil during forest formation are still lacking.

Scots pine (*Pinus sylvestris* L.) grows in the zone of hemiboreal forests of the Baltic region, and occupies 34.5% of all forested area in Lithuania [16]. As early succession species, Scots pine has wide ecological plasticity, but is light demanding. In Lithuania, its prevalence depends on edaphic conditions; therefore most of the stands grow on nutrient-poor soils. The local forestry practice shows that clear cuttings are the major disturbance in Scots pine forests in Lithuania.

This study aimed to assess organic carbon and nitrogen concentrations and their change in the mineral topsoil layers (0-10 cm, 10-20 cm and 20-40 cm) during the stand rotation period up to mature stand.

#### **MATERIAL AND METHODS**

The study was carried out in Trakai in south-western Lithuania (Latitude: 54°38'16.19"N; Longitude: 24°56'3.59"E) at the land of Trakai Regional Division of State Forest Enterprise. The mean annual temperature was 6.5°C, and the mean annual precipitation was 686 mm.

Five different Scots pine (*Pinus sylvestris* L.) sites of age: 0 – fresh clear-cutting, 8-, 30years old, and mature stand (101-years old) were selected subjectively to represent typical Scots pine stands within this area. The five sites were all located within a radius of about 2 km. The forest type was *Pinetum vacciniosum* for all plots, and the forest site type was Nb – oligotrophic mineral soil of a normal moisture regime, according to the Lithuanian classification [17]. The soils were classified as well-drained *Haplic Arenosol* and consisted of coarse sand with low (<5%) clay+silt content [18,19]. The following species prevail in the ground vegetation cover: dwarf shrubs – *Vaccinium myrtillus, V. vitis-idaea, Calluna vulgaris,* and herbs –*Luzula Pilosa* (L.) wild, *Pteridium aquilinum* Kuhn, *Lycopodium clavatum* and mosses – *Pleurozium schreberi, Hylocomium splendens, Ptilium crista – castrensis, Polytrichum juniperinum.* 

Soil samples of the mineral topsoil layers of 0–10 cm, 10–20 cm and 20–40 cm depths were collected using a metallic soil auger. The samples were collected in August 2020. Three composite samples were combined from 10 subsamples collected systematically in each sample plot (the distance between the sampling points was at least 5 m).

Soil  $pH_{CaCl2}$  and concentration of organic carbon (C), total nitrogen (N) and mineral nitrogen (N<sub>min</sub>) were estimated. For chemical analyses, the mineral soil samples sieved through a 2 mm sieve. Indicators, determined in the mineral topsoil samples were: pH - in a 0.01M CaCl<sub>2</sub> suspension (ISO 10390:2005); organic carbon (C) concentration was determined with a Heraeus apparatus (ISO 10694, dry combustion at 900°C), and total nitrogen (N) was analysed using the Kjeldahl method (ISO 11261). Concentrations of mineral N were determined by the spectrometric method (ISO 14256-2) in 1 M KCl extraction: NH<sub>4</sub>-N using sodium phenolate and sodium hypochlorite, and NO<sub>3</sub>-N using sulphanilamide. Mineral N (N<sub>min</sub>) was determined

by summing up NH<sub>4</sub>-N and NO<sub>3</sub>-N. Soil chemical analyses were conducted in the Agrochemical Research Laboratory of LAMMC.

For data comparison, the one-way analysis of variance ANOVA post-hoc LSD test was used. Data are presented as means  $\pm$  standard error (SE). Statistical analyses were conducted using STATISTICA 12.0 (StatSoft. Inc, 2007) software, and the level of significance of p < 0.05 was used in all cases.

### RESULTS

The pH<sub>CaCl2</sub> values in the mineral 0–10 cm topsoil showed the most significant variation between different age groups' sites (Fig. 1). The highest pH values (pH<sub>CaCl2</sub> 3.7–3.8) were obtained in the fresh clear-cutting and 8-years old Scots pine plantation. The lowest pH values (pH<sub>CaCl2</sub> 3.6) were found in the 30-years old plantation and the mature Scots pine stand of 101-years old. However, no significant differences between the sites were found in deeper topsoil layers. The pH values were in narrow ranges, i.e. pH<sub>CaCl2</sub> 3.9–4.1 in 10–20 cm; and pH<sub>CaCl2</sub> 4.1–4.3 in the 20–40 cm topsoil layers.

The data given in Fig. 2 shows the concentration of organic carbon (C) in fresh clearcutting, 8- and 30-years old Scots pine plantations and mature stand of 101-years old. The highest C concentration was found in the 0–10 cm topsoil of a 30-years old Scots pine plantation. This value was 1.4 times higher than C concentration in the mature Scots pine stand. However, in 10–20 cm topsoil layer of 30-years old plantation, C concentration was 1.2 times lower than the mature stand. No site effect was obtained in the deeper 20–40 cm topsoil layer.



Fig. 1. The mean pH<sub>CaCl2</sub> values in fresh clear-cutting, 8- and 30-years old Scots pine plantations and 101-years old mature stand. Bars show the mean  $\pm$  SE (n = 4). Different letters a and b indicate statistically significant differences between the sites (p < 0.05).



Fig. 2. The mean concentration of organic carbon (C, %) in fresh clear-cutting, 8- and 30years old Scots pine plantations and 101-years old mature stand. Bars show the mean  $\pm$  SE (n = 4). Different letters a and b indicate statistically significant differences between the sites (p < 0.05).

Total N concentration was 1.3 times higher in the 0–10 cm topsoil layer of 30-years old plantation than in the mature forest (Fig. 3a). In deeper 10–20 cm and 20–40 cm topsoil layers, total N concentration increased in the fresh clear-cutting and 8-years old plantations, and the values differed 1.2 times and 1.3–1.5 times, respectively.

The data clearly showed a significant increase of mineral N concentration in the fresh clear-cutting, especially in the 0–10 cm topsoil layer (Fig. 3b). The difference from the Scots pine mature stand comprised by 7.0 times, 3.6 times and 1.4 times for 0–10 cm, 10–20 cm and 20–40 cm layers, respectively.



Fig. 3. The mean concentration of total nitrogen (N, %) (a) and mineral N (Nmin, mg/kg) (b) in fresh clear-cutting, 8- and 30-years old Scots pine plantations and 101-years old mature forest. Bars show the mean  $\pm$  SE (n = 4). Different letters a and b indicate statistically significant differences between the sites (p < 0.05).

The C:N ratios ranged between 25.5:1 and 37.9:1 in the topsoil of 0-40 cm depth. The C:N ratios were generally high in the 20–40 cm topsoil of 30-year-old plantation (C:N 37.9:1) and mature forest (C:N 34.9:1). The C:N ratios were similar in the 0-10 cm and 10-20 cm topsoil layers of fresh clear-cutting and 8-years old plantation.

#### DISCUSSION

Typically, during the clear-cutting of a mature forest stand, when all logging residues are removed compared with stem only harvesting, soil C and nutrient stocks and concentrations can be reduced [20, 21]. Such operation can cause nutrient imbalances or C and N depletion in the site. It is also important that clear-cutting has a drastic impact on vegetation cover; therefore, vegetation's nutrient consumption is significantly reduced [4, 22, 23]. The previous studies indicated that the nutrient release is often accelerated after the clear cuttings where logging residues were removed [24, 25].

However, controversial findings on harvesting impact on soil chemistry still exists. For example, [2] found little change in mineral soil C after clear-cutting, but [26] found a significant reduction in forest soil C in mineral soil. The impacts of harvesting on soil C and N depend on soil layers and element concentrations or stocks [27 - 29].

The changes are expected for a certain time. In this study, the mineral topsoil changes were analyzed in four-time intervals (clear-cutting, 8-, 30-years old Scots pine stands and mature forest stand) per whole stand rotation (101 years). The main differences were obtained between the clear-cutting sites and mature Scots pine stand, especially in the case of mineral N concentration, which significantly increased next year after clear-cutting. As noted by [30], the fastest decomposition of organic matter and nutrient release in the mineral soil of clear cuttings is expected during the first three years after clear cuttings. The level of nitrates stabilizes after four or five years, but the leaching of organic C and other nutrients could be fixed up to ten to twenty years after clear-cutting [2, 4, 9, 23]. The latter effect in our study's case could have been likely occurring between 8 and 30 years of stand formation.

Our results showed that clear-cutting reduced the C:N ratio, and this finding was less compared with the data obtained in the previous studies. For example, [31] showed that whole-tree harvesting increased C:N ratios in the 0–5 cm mineral soil layers and this effect in the mineral soil was detected 16 years after felling. [32] The harvesting increased the mineral soil C and C:N ratio but reduced mineral soil N stock.

This study showed the impacts of harvesting on soil C and N concentrations in mineral topsoil up to 40 cm depth. The mentioned changes were weaker than those possibly obtained in the forest floor, as shown by previous studies [33]. This could be mentioned as one of the limitations of this study, and chemical differences in forest floor will be investigated in the near future.

#### CONCLUSIONS

A significant increase of pH values in fresh clear-cutting Scots pine sites was obtained only up to 10 cm depth of mineral topsoil. The total organic carbon concentrations remained relatively constant after clear-cutting but increased in 0–10 cm mineral topsoil layer of 30-years old stand. The concentration of total N and mineral N varied between the sites of different age and topsoil depths. The highest mineral N concentration was found in 0–10 cm in the fresh clear-cutting, which consequently decreased going deeper up to 40 cm depth.

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## SCREENING OF CITRUS EPIPHYTIC BACTERIA AGAINST POST-HARVEST DISEASE

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#### ABSTRACT

Citrus fruits are vulnerable to the postharvest decay caused by *Penicillium digitatum*, the common agent of green mold. Usage of conventional chemical pesticides over the past hundred years harmed the environment, harmed human health and strongly influenced resistance development in target pathogens. Therefore, novel, safer, and more environmentally-friendly pesticides are urgently needed. One of the novel methods to help with the biocontrol of this disease is attributed to the epiphytic microbial community associated with the orange plants. In this regard, 23 epiphytic bacterial isolates were obtained from six healthy citrus fruit. In screening bioassays, three species in the genera *Bacillus* sp., *Pseudomonas* sp., and *Streptomyces* sp. were the most effective bacteria against *P. digitatum*. The supernatant of these bacterial cultures also displayed a clear *P. digitatum* growth inhibition. Out of three tested bacteria genera, *Bacillus sp.* was the most effective bacteria against *P. digitatum*. The strain *Bacillus cereuse* H7 was further identified by 16S rRNA sequence analysis. HPLC analysis of *Bacillus cereuse* identified the inhibiting antibiotic substance as iturin A. It is worth mentioning, the semicommercial application of these citrus epiphytic bacteria improved orange fruit quality and therefore, could be considered as an appropriate alternative to chemical control of orange postharvest diseases caused by *P. digitatum*.

Key world: Bacillus cereus, Biocontrol, Epiphytes, Iturin A, P. digitatum

## **INTRODUCTION**

Citrus is an important fruit crop worldwide, especially in tropical and subtropical regions around the world. Citrus fruit also contains many nutritional components beneficial to human health. Postharvest diseases cause considerable losses to harvested fruits and vegetables during transportation and storage(1). Postharvest green mold is the main fungal agent known to cause citrus fruit decay, which leads to huge economic losses worldwide every year and can account for up to 90% of the total citrus postharvest losses, especially in arid zones and subtropical climates (2). Since the beginning of the 1960s, treatments based on chemical fungicides as the main method of reducing postharvest fruit losses have obtained satisfactory results. However, in the last few decades, stricter regulatory policies have started to be imposed on their use (3). It is well-documented that the treated fruit surfaces are completely covered by the fungicides, and their residues remain on the fruit surface for a long time (4). Therefore, the application of chemical fungicides has been restricted due to concerns about pesticide residues, environmental pollution, and pathogens resistance. It is urgent to search for effective, eco-friendly methods of disease control to replace or reduce the use of harmful chemical fungicides (5). The use of biological agents in postharvest decay control as an alternative to synthetic fungicides has been

more attractive in the last two decades, and several studies have demonstrated the potential of certain microbial agents(6 and 7). Many reports demonstrated successful control of postharvest pathogens on citrus fruits by using antagonistic bacteria, including *Paenibacillus brasilensis*, *Bacillus subtilis*, *Burkholderia gladioli* pv. *agaricicola*, and *Streptomyces* sp. (8, 9 and 10).

This study aimed to evaluate the antifungal activities of citrus epiphytic bacteria which live non-parasitically on the surface of citrus fruit against orange post-harvest green mold disease. Molecular identification of the most effective epiphytic bacteria and antifungal bioactive compounds of the representative strain was verified.

#### METHODOLOGY

#### **Isolation of Target Pathogen:**

Five main fruit markets were patrolled in Golestan Province of northern Iran to select infected fruits. *Penicillium digitatum* was isolated from infected Thompson navel' orange fruits showing dark brown rot symptoms. Healthy oranges were also collected to serve as controls. The *P. digitatum* isolate used in this study was obtained from naturally decayed orange fruits. Small pieces of fruit tissue, previously surface-disinfected with 90% ethanol, were aseptically excised from the advancing edge of the rot and transferred to Petri plates containing potato dextrose agar (PDA) amended with 1 ml of lactic acid (80%) per liter. After a 4-day incubation period at 25°C, plates were examined under a stereomicroscope to determine colony morphology. The pathogen used in this work was the most aggressive one in our collection and produced the largest lesions on inoculated fruit in the pathogenicity test. This fungus was purified and maintained on PDA and stored at 4°C, with periodic transfers through citrus fruit to maintain its aggressiveness.

#### **Penicillium** Conidial Suspension:

To produce inoculum, a strain of *P. digitatum* was cultured on PDA dishes for 8 days at  $24 \pm 1^{\circ}$ C. The surface of the *P. digitatum* colony was washed with 6 mL of sterile distilled water containing 0.1% (v/v) tween 80. The resulting suspension was filtered through two layers of sterile gauze and spores were counted. A suspension with a concentration of  $5 \times 10^4$  conidia/ml was used for all *in vitro* and *in vivo* trials.

## **Isolation of Epiphytic Bacteria Obtained from Orange Fruits**

Epiphytic bacteria were isolated from 6 healthy Thompson navel orange fruits. The samples were cut into pieces (5×5 mm) and immersed in 0.6% NaOCl for 3 min and 70% ethanol for 1 min. The specimens were then washed three times in sterile distilled water. The surface-sterilized samples were then transferred in tubes containing 5 ml D.H<sub>2</sub>O. One loopful from each sample suspension was streaked on nutrient agar (NA) and incubated at room temperature for 72 h. Single colonies were re-streaked on new NA plates to obtain pure cultures. The bacterial isolates were stored on NA slants at 4°C and in nutrient broth (NB) mixed with 25% glycerol at  $-20^{\circ}$ C for further study.

## Screening For Inhibitory Effects of Epiphytic Bacteria on P. digitatum

Screening for the inhibitory effects of epiphytic bacteria against *P.digitatum* was performed using a dual culture technique. Cell suspension of P.digitatum was swabbed on the surface of NA, and then each epiphytic bacteria was streaked with four lines (2 cm long),

coupled with opposites at a 1 cm distance from the four edges of the plates and incubated at room temperature for 48 h. The inhibition zones around the four streaks of each epiphytic bacteria were measured. The epiphytic bacteria that displayed antagonistic effects on *P.digitatum* were further assessed by the agar well diffusion method(11). After swabbing *P.digitatum* on the NA plates, four wells (5 mm) were made on each plate of the NA, and then  $30 \ \mu l \ (10^8 \ CFU/ml)$  from each epiphytic bacterial suspension was added into the wells of each NA plate. All plates were incubated at room temperature for 48 h and bacteria with inhibition zones above 5 millimeters were selected.

## In Vitro Bioassay for Biocontrol of the Fungus On Orange Fruits

The wounded fruits (5 mm wide × 4 mm deep) were made using a sterile needle at the equatorial side were inoculated with 20  $\mu$ L of bacterial suspensions at concentrations of 10<sup>6</sup>, 10<sup>7</sup>, 10<sup>8</sup>, and 10<sup>9</sup> CFU/mL. Two hours later, wounded fruits were further treated by the same volume of 1×10<sup>4</sup> spores/mL conidial suspension of *P. digitatum*. Wounds treated with 20  $\mu$ L SDW before pathogen inoculation served as a control. All treated fruits (with four replicates) were packed and placed in a constant temperature and humidity incubator at 20°C under 90% RH for 8 d. The lesion diameters were determined by taking the mean of the horizontal and vertical diameters of each lesion, and the disease incidence was calculated by the number of infected wounds. Any fruit wound with visible mold growth was considered to be infected.

## **Identification of Selected Effective Bacteria**

Three representative antagonists were identified by classical and PCR-based methods. The key morphological, physiological and biochemical characteristics were comprised of Gram staining, cell shape, pigmentation on KB, endospore formation, O/F and oxidase, and catalase tests, potato soft rot, and HR on tobacco leaves. DNA extraction of the selected bacteria was performed by homogenization using the boiling method, followed by the manufacturer's protocol. In brief, few colonies of each selected bacterium were transferred into 1.5 ml Eppendorf tubes containing 100 µl of buffer A (100 mM Tris-HCl, 1M KCl, and 10 mM EDTA). The Eppendorf tubes were then centrifuged at 12,000 rpm for 10 min. The supernatants were transferred to new Eppendorf tubes to be used as DNA templates. The PCR amplification of 16S rRNA genes was carried out in a PCR thermal cycler (Bio-Rad My cycler) using a SINA Extraction kit: Cat.No.DN8115C and universal primers, Forward GEN (27F): 5'AGAGTTTGATCCTGGCTCAG-3' and Reverse (1390R): 5'-GACGGGCGGTGTGTACAA -3'. PCR reaction conditions were as follows: 94°C for 2 min, followed by 25 cycles of denaturation at 94°C for 1 min, annealing at 52°C for 1 min, and extension at 72°C for 3 min, before a final elongation at 72°C for 20 min. Approximately 1500 bp in length DNA bands are separated on a 0.8% agarose gel. DNA sequences of the PCR products were obtained from Macrogene Inc. and were compared with the sequences deposited in GenBank by the BLAST (Basic Local Alignment Search Tool) program (NCBI, http://blast.ncbi.nlm.nih.gov/).

## Extraction and Evaluation of Bioactive Compounds from Selected Epiphytic Bacteria:

The selected most effective bacteria were cultured in NB and grown in nutrient broth by shaking 120 rpm for 24 hr at 30° C. 5 ml of each culture was inoculated in 500 ml of TSB and incubated at 150 rpm for 72 hr at 30° C. The culture supernatant total (5 liters) was obtained by centrifugation of the bacterial culture for 20 min at 10,000 rpm and subsequently incubated overnight at 4°C after adjusting its pH to 2.0 by adding HCl. Precipitates formed in the acidified culture supernatant were harvested by centrifugation for 20 min at 10,000 rpm and subsequent

washing with acidic distilled water (pH 2.0). The precipitates were dissolved in methanol and concentrated by a rotary vacuum evaporator. The overall process for the isolation of antifungal compounds was done accordingly (12).

#### **Statistical Analysis:**

All the experiments were conducted twice using CRBD, and each treatment was replicated three times. Statistical analysis was performed with one-way analysis of variance (ANOVA) test using SPSS Version 19.0 software. All experimental data were expressed as mean  $\pm$  standard deviation (X  $\pm$  SD). Differences were considered to be statistically significant when P< 0.05 according to Dunnett's test.

## **RESULTS AND DISCUSSION**

## **Characteristics and Pathogenicity Test of Fungi Isolated from Infected Orange Fruits**

Colonies of the fungi isolated from a decayed portion of orange fruits were a velvety to deeply floccose texture with color yellow-green but ultimately turned olive due to conidial production and completes its growth cycle within two days which was following the general characteristics of *Penicillium digitatum*. Colony texture is velutinous with no exudate droplets (13). According to the morphological and cultural characteristics and pathogenicity test, the fungus was identified as *Penicillium digitatum*.

#### Characteristics and Pathogenicity Test of Most Effective Epiphytic Bacteria

Based on certain physiological and biochemical characteristics, the isolates were tentatively identified at their genus level: *Bacillus*, *Streptomyces*, and *Pseudomonas*. *Bacillus* spp. was the most effective antagonists against *P.digitatum*.

The *Bacillus* colonies were usually whitish to cream on NA. Biochemical properties of *Bacillus* H7 were in accordance with the chacteristics of *B. cereus* described by Laurentiu et al., 2014 (21). On the other hand, most of *Streptomyces* isolates showed a white-colored colony surface and a dry and powdered texture, and some colonies were able to produce pigments with the same characteristics (15). Some *Pseudomonas* isolates produce fluorescent pigment on KB agar. *Pseudomonas* isolates test for aerobic, oxidase-positive, catalase-positive were positive and HR on tobacco and potato soft rot test were negative for all strains *Pseudomonas*.

## In Vitro Screening For Antagonisitc Activities Epiphytic Bacteria Against P. digitatum

Twenty three isolates of epiphytic bacteria were collected from the six healthy orange fruits. 14 isolates of 23 isolates could inhibit *P.digitatum* in a dual culture technique. These were the most effective bacteria against *P. digitatum*. The degree of inhibition zones varied between  $5.0 \pm 0.5$  mm and  $15.6 \pm 0.2$  mm (Table 1). Three of the most important strains with maximum inhibitory effects were identified as *Bacillus* sp. H7(15.6  $\pm$  0.2mm), *Streptomyces* sp. H16 (9.0  $\pm$  0.4 mm) and *Pseudomonas* sp. H8 (6.3  $\pm$  0.2 mm), respectively. As shown in table 1, *Bacillus* sp. H7 was the most effective bacteria against *P.digitatum*. Many studies are demonstrating the impact of biological agents in postharvest disease control. Mycelial growth inhibition and reduction in spore germination of *Penicillium* sp. by *Bacillus subtilis* and *Agrobacterium radiobacter* have been also reported(10). The positive effect of the *Pseudomonas fluorescens* in the control of citrus green mold caused by *Penicillium digitatum* and the possible modes of action were evaluated and reported (16).

<b>Bacterial isolates</b>	Diameter of inhibition zones (mm)
Bacillus sp. H2	$13.6 \pm 0.3^{\circ}$
Bacillus sp. H7	$15.6\pm0.2^{a}$
Bacillus sp. H19	$14.2 \pm 0.2^{b}$
Bacillus sp. H21	$11.9 \pm 0.2^{d}$
Pseudomonas sp. H3	$6.1 \pm 0.4^{h}$
Pseudomonas sp. H8	$6.3\pm0.2^{ m h}$
Pseudomonas sp. H13	$4.1\pm0.5^{\mathrm{i}}$
Streptomyces sp. H6	$7.0\pm0.5^{ m g}$
Streptomyces sp. H10	$8.8\pm0.3^{\rm f}$
Streptomyces sp. H16	$9.0\pm0.4^{e}$

 Table 1: Average diameter of inhibition zones (mm) of bacterial isolates obtained by the agar diffusion method on *P.digitatum*

Diameter of inhibition zones with  $\pm$  standard error of means (n = 4), and different superscript letters indicated significant differences (P < 0.05) according to Duncan' multiple range test.

# Screening For Antagonistic Activities of the Epiphytic Bacteria Against *P.digitatum* in Fruit Bioassays

As mentioned earlier, 60% of the epiphytic strains isolated from healthy orange fruits could control post harvest citrus decay caused by *P. digitatum* both in vivo and laboratory fruit bioassays. This is consistent with the results of many previous reports of fungal control of bacteria(14,15,16). It is well-documented that bacterial isolates showed more or less antifungal activity against the fungal pathogens and have been widely used in biocontrol strategies for plant pathogens.

In this study, three strains of *Bacillus* sp. H7, *Pseudomonas* sp. H8, and *Streptomyces* sp. H16 had the highest inhibitory potential for fungal growth in two levels of culture medium and fruit bioassays.

The maximum antagonistic activities were observed by *Bacillus* spp. particularly *Bacillus* sp. H7. The disease incidence was reduced from 83.50% to 23.00%, and the lesion diameter was reduced from 3.06 cm to 1.17 cm, respectively compared with controls (Fig 1). *Bacillus* species are the more attractive and effective due to their resistance to adverse environmental conditions and ability to control a broad range of pathogens. The bacilli can also produce different antimicrobial substances that confer protection and act as biological agents (18). Species belonging to this genus can play a role as human pathogens, whilst others promote plant health and development (19). Some strains of *Bacillus* spp. also induce systemic resistance of the host plants (14).



Fig 1. Effect of selected epiphytic bacteria in controlling orange decay caused by *P. digitatum*. C: control, BH7: *Bacillus* sp. H7, PH8: *Pseudomonas* sp H8, SH16: *Streptomyces* sp. H16. Columns with different lowercase letters within are significantly different at the P < 0.05 level by Duncan's multiple range test.

The second group of bacteria with antagonistic activity against *Penicillium digitatum* belong to the species of the genus *Pseudomonas*. Their antagonism over fungal phytopathogens such as *Fusarium, Curvularia, Helminthosporium*, and *Aspergillus niger* has been approved for a long (15).

The lowest effect on disease incidence and the lesion diameter was observed with *Pseudomonas cepacia*. Its effect in controlling wounded orange fruits has been confirmed (20). Among *Pseudomans* spp., most antagonists were related to the biovars of *P. fluorescens* (16).

#### **Molecular Identification of Selected Effective Bacteria**

The 16S rRNA genes approximately 1500 bp long were amplified by *Bacillus* sp. H7, *Pseudomonas* sp. H8, and *Streptomyces* sp. H16 (Fig 2).

In BLAST of target gene sequencing of most effective bacteria, *Bacillus* sp. H7 shared 99% homology with *B. cereus* (GenBank Accession No. JF895480.1)



Fig 2. A PCR amplification product of 1500 bp for three selected effective bacteria. strains on agarose gel. Lane designations: M, 100 bp ladder, C: control, H7: *Bacillus* sp. H7, H8: *Pseudomonas* sp H8 and H16: *Streptomyces* sp. H16.

#### Analysis of standard iturin A and extracted antifungal agents of B. cereus

The most commonly employed technique for the detection of antifungal agent produced by *Bacillus* spp. is Reversed-Phase Chromatography, which results in separation of each lipopeptide structure based on polarity (22). Separation of standard iturin and correspond isomers of the extracted materials of *B. cereus* have been achieved with methanol-water (65% v/v) as isocratic elution. As shown in Fig (3) standard iturin A contains 1 high peak at retention time range; 0-2.5. The purified crudes of *B. cereus* had also the main peaks at 0-2.5 retention time range. HPLC had also the same number of main peaks (1.585) which were observed at elution times comparable with those observed for standard iturin A and they might be the isomers of iturin A.



Fig3: (a): chromatogram of standard iturinA, (b): analysis of iturin methanolic extract of iturin *Bacillus cereus* 

#### CONCLUSIONS

This study showed that epiphytic bacteria mainly *Bacilli*, *Streptomyces*, and *Pseudomonas* spp. which have been isolated from orange fruits have strong antifungal properties against *Penicillium digitatum* both in vitro and in fruit bioassays. The antifungal compound produced by *Bacillus cereus* sp. H7 is detected as iturin A. These bacteria could be considered as an appropriate alternative to the chemical in the control of orange postharvest disease caused by *P. digitatum*.

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## USE OF TERRESTRIAL LASER SCANNER IN SHORT ROTATION CROPS FOR ABOVE-GROUND WOODY BIOMASS ESTIMATION

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#### ABSTRACT

Short-rotation crops (SRC) have become an important source of woody biomass around the world [1, 2]. The expansion of the SRC is supported by environmental policies and economic considerations: wood for cellulose or biomass for energy [3]. A precise estimate of biomass production is necessary for the sustainable planning of forest resources and for the exchange of energy in ecosystems. The use of the terrestrial laser scanner (TLS) in estimating the production of above ground wood biomass (AGWB) of short rotation crops brings an important technological leap among indirect (non-destructive) methods. TLS technology is justified when destructive methods become difficult to carry out and allometric equations do not give accurate information [4]. The main purpose is to estimate the biomass productivity on tree parts in short rotation forestry with TLS technology, comparing the results with the gravimetric method. Measuring the hybrid poplars crops by TLS may have the following consequences: (i) higher accuracy of the estimate of biomass production in the SRC; (ii) cost and time effective measurements over the biomass of tree parts; (iii) new and validated allometric equations for SRC in NE Romania. Through the research protocol, the use of TLS for comparison with the gravimetric method will contribute to the development of knowledge in the field of hybrid crops.

Keywords: above-ground woody biomass (AGWB); short rotation crops (SRC); terrestrial laser scanner (TLS).

## **INTRODUCTION**

## The importance of assessment of biomass productivity in short rotation crops (SRC) with terrestrial laser scanner (TLS)

The poplar crops area is growing in Europe, exceeding 800 thousand ha, of which 21% represents systems of short rotation crop production [5, 6]. The system of SRC, is an efficient alternative of bioenergy production under a temperate climate [7, 8].

In Romania, the interest for SRC has increased due to modern cultivation technologies [9, 10]. At the same time, Romania offers a high potential for marginal land suitable for planting of these crops [11, 12], an aspect that has attracted the attention of many investors. Thus, starting with 2009, a private investor has installed significant surfaces of SRC in NE Romania [13, 14]. Currently, in this area are installed more than 800 hectares of SRC. These prospects are particularly of interests to private sector, which finds in short rotation opportunities of developing and investing on short and medium terms.

The right estimation of tree above-ground wood biomass (AGWB) and stem volume is needed both for sustainable planning of forest resources and for optimizing of energy and nutrients flows within terrestrial ecosystems. Moreover, the EU Framework convention on climate change and for the Kyoto Protocol recognize the importance of forest carbon stock in relation to the atmospheric CO<sub>2</sub> concentration [3]. On the other hand, the Romanian policy regarding the "System of tracking wood material" (SUMAL 2.0), is an issue for private investors because for many new hybrid clones there are not any coefficients for a real volume estimation and the *Ministerial Order 1323/2015* (technical rules) does not offer proper volume equation.

Biomass production can be estimated by direct and indirect methods. Recently, the development of terrestrial laser scanning (TLS) has made possible to map a three dimensional plot or a single tree with higher accuracy [15, 16]. The TLS is a technique introduced less than ten years ago as an innovative concept in tree measurement [17, 18].

Using TLS on biomass estimation per tree parts (total, branches and stem) is a topic of great interest for researchers, foresters and private investors. TLS technology is justified when destructive methods become difficult to carry out and allometric equations do not give accurate information.

### The goal

The goal of this study is to highlight the potential of TLS technology in above ground wood biomass estimation of hybrid poplar clones in short rotation crops.

The technical point addressed in this paper is to present theoretical aspect of: (*i*) evaluation of above ground wood biomass using TLS, (*ii*) assessment of stem quality in short rotation forestry using TLS, and (*iii*) development of calibrated allometric equations in short rotation crops using TLS technology.

#### METHODOLOGICAL APPROACH

#### Site description

The researchers are carried out in NE Romania in the hilly area (346 m elevation). The climate is temperate continental, with annual temperature of 7°C and rainfall about 550 - 600 mm [19, 20]. The soil is *Faeoziom cambic*, moderately acidic with highly trophic for all selected crops [21, 22]. There are no stational conditions differences between the selected crop areas and have been maintained under the same culture technology [1].

#### **Experimental design**

For the most productive hybrid poplar clone (AF8 – *P. x generosa 103-86 x P. trichocarpa PEE* and Pannonia – *P. x euramericana*), three plots for different production cycles ranging from 5 to 7 years are delimited in crops. The size of the plots is approx. 81 m<sup>2</sup>, including approx. 10 trees · plot<sup>-1</sup> on two rows, installed for a density of 1667 trees · ha<sup>-1</sup> (planting at 3 x 2 m). As planting material are used rods (long cuttings) of 2 m. For the selection of the total 18 sample plots, marginal influence will be avoided (*Table 1*).

Planting characteristics	Planting density $-3 \ge 2 \le m - 1667$ trees $\cdot ha^{-1}$			
Planting year	2015	2016		
Growing seasons (cycle)	6 / 7	5		
Inventory stage	2021 / 2022	2021		
Plant material	rods - 2 m length	rods - 2 m length		
Hybrid poplar clones:	Numbers of sample plots (with approx. 10 trees plot <sup>-1</sup> )			
AF8	3	3		
	47°51'19.51"N	47°51'21.40"N		
	25°59'13.54"E	25°59'30.23"E		
Pannonia	3	3		
	47°51'19.67"N	47°50'39.60"N		
	25°59'27.52"E	26° 3'40.73"E		

Table	18.	Characteristics	of	sample	e plots
I aoie	10.	Characteristics	O1	Sumpr	e proto

The propagating material (rods) was installed in the field at a depth of 0,6 - 0,7 m in the spring of each year in which the installation was made, according to the culture technology adopted [23, 24].

#### Methods of data collection

#### Evaluation of above ground wood biomass

TLS scans are carried out beyond the vegetative period, when the hybrid poplars will not present leaves (November – April) in 2021 and 2022 according to inventory stage (*Table 1*). The Z+F Imager 5010 Scanner (Zoller and Fröhlich, Wangen, German) is used to obtain field points clouds, with the necessary additional materials: batteries (or generator), spherical targets (of 200 mm), cables, etc. With the necessary methodological requirements and precautions for practical application [4, 25]. The appropriate weather conditions (with low wind intensity, temperatures more than -10°C and no rain or wet bark) will be monitored to perform scans for the capture of fine branches.





A minimum of 6 scanning's is used for each plot, with 8 targets of 20 cm (*Figure 1*). The estimated scanning time for a single plot is about 3-4 hours  $\cdot$  person<sup>-1</sup> (with transport equipment, installation targets, scanning and equipment collecting). Each plot is materialized on the field with metal corner.

All trees within the plots are tagged with numbers and they are measured: stem diameters, heights and crown diameters (for validating equations and checking stem quality). After scanning activities, the destructive method will be used to validate biomass production. For biomass productivity, a series of direct measurements (by weighing) on the green mass on the parts of the trees (total, stem and branches) will be used. According to the working structure presented (Table 1), the data are completed in the next vegetative inactive period. Sample plots are scanned, inventoried, harvested and weighed on tree parts, comparing the TLS method with the gravimetric method. Density estimation will be done through the *gravimetric method* in the laboratory, on harvested samples, as follows: wooden rounds from stem and a representative branch [26, 27].
## Assessment of stem quality in short rotation forestry using TLS

The quality of the stem will be determined in relation to the Dimensional sorting table (*STAS 1040-85*) and grades needed for wooden boards. The stem will split into two grades: (*i*) stem log with a minimum diameter of 8 cm at the thin end (used for OSB production), and (*ii*) wood for biomass (for co-generation) with diameters less than 8 cm [1]. The validation of the distribution on the log assortments will be made by shape indices (using caliper measurements along the tree stem). The defects of wood will also be taken into account.

## Allometric equations in short rotation crops using TLS technology

The TLS results will be used to calibrate the allometric equations obtained by destructive methods for the same conditions related to: crops characteristics, area and inputs. For high accuracy of tree parts, it is necessary to generate a model based on the three measurable dendrometric features, including the diameter of the crown (on two perpendicular directions) in addition to the stem diameter and tree height.

## Methods of points cloud processing

Data processing involves: co-registration data is carried out on fixed spherical targets (200 mm), filtering data and extracting necessary parameters is done by using *ZF Laser Control*, *CloudCompare*, *R* and *MathLab software* [4]. Long working time, it is necessary for points filtering and error fixing (solving "phantom points"), until tree individual selection (Figure 2). The *Autostem application (Treemetrix)* based on multiple scans will determine the stem and branches volume. Volume will be estimated directly from the measurements, while the determination of biomass will require wood density on each part tree [25, 28]. Scanning the branches will be based on a quantitative model taking into account the obstruction [29, 30].



Figure 21. Point cloud selection correspondent of a trees, until their individual materialization. Processing data in *CloudCompare 2.12 (left) and Z+F LaserControl 9.0.2 (right).* 

The individual production of AGWB will be extrapolated to the area unit (dry mass t  $ha^{-1}$ ). The TLS results will be used to calibrate the allometric equations obtained by destructive methods and for the same conditions related to crops characteristics (clone or rotation/ cycle for the same density), area (conditions of vegetation) and inputs.

## CONCLUSIONS

In Romania, TLS technology has never been used in short rotation wood crops, the few cases in forest inventories [25, 31]. In this regard, getting fast data at minimal cost became a necessity for stakeholders, especially when this is performed with great accuracy. Compared to the other methods, the use of TLS for biomass (volume) in such crops opens new paths for research. The gain will be both for the scientific side and for the investors in the SRC (economic side). The novelty is the development of the scanning protocol with TLS.

Measuring the hybrid poplars crops by TLS may have the following consequences: (*i*) higher accuracy of the biomass production estimation in the SRF; (*ii*) cost and time effective measurements over the biomass of tree parts; (*iii*) new and validated allometric equations for SRC in NE Romania, and (*iv*) robust instrument for industry to estimate biomass.

## ACKNOWLEDGEMENTS

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# **CONFERENCE PAPERS**

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# PHOTOPOLYMERIZATION AS A NON-TOXIC, ENVIRONMENTALLY FRIENDLY METHOD FOR OBTAINING INNOVATIVE DENTAL FILLINGS

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#### ABSTRACT

The light-initiated process plays an increasingly important role in biomedical applications for the production of photocurable dental fillings. The use of photochemically initiated polymerization to obtain dental composites enables the use of unique and innovative features of this method. The most important are: short curing time of the composition (up to a few seconds); carrying out the reaction at room temperature; low energy consumption, spatial resolution (polymerization only in the exposed areas). Nevertheless, many different factors, such as the selection of appropriate monomers, initiators, inorganic fillers, curing time, type of radiation and light power, influence the quality of the composite obtained.

In this work, influence of different factors such as weight ratio of BisGMA and TEGDMA monomers, amine concentration, type of amine, type of diode on properties of standard dental light-cure composite resins were studied. Completely new, safe initiating systems intended for the production of a new generation of dental composites polymerizing via cationic mechanism, characterized by reduced polymerization shrinkage were also presented. Conversion rates were investigated using the Real-Time FT-IR technique. The article shows that the highest conversion rates were obtained for a dental composition composed of camphorquinone (CQ) and ethyl 4-(dimethylamino)benzoate (EDB) in molar ratio 1: 2 and bisphenol A-glycidyl methacrylate (BisGMA) and triethylene glycol dimethacrylate (TEGDMA) monomers in weight ratio 7: 3.

Keywords: photopolymerization, photoinitiators, cationic polymerization, photocurable dental resins

## **INTRODUCTION**

Photopolymerization is gaining popularity because it is an environmentally friendly and safe method for production of different polymer coatings. Moreover, it has plenty of benefits. The primary advantage of the photopolymerization over other methods used for preparation of polymer coatings is its speed. Photo-curable compositions are transformed from a liquid state into a fully cross-linked solid within seconds. The photopolymerization ensures no emission of any volatile solvents to atmosphere. Moreover, this process provides several other advantages, e.g.: ambient temperature operation, solvent free formulations, and low energy consumption [1-2]. Because of many advantages, photopolymerization is used in many scientific disciplines, e.g. in coatings industry for preparation of coating materials for automotive and furniture industries, in polygraphic industry (for making colour imprints on different materials) or even in medicine for preparation of polymeric hydrogels. Moreover, the photopolymerization ensures [3-4].

The most commonly used photo-cured dental materials are dimethacrylic compounds, which guarantee the production of high crosslinking networks. The most common monomers used for dental applications are bisphenol A - glycidyl methacrylate (BisGMA) and triethyleneglycol dimethacrylate (TEGDMA). BisGMA is very popular for the production of dental composites. Due to the presence of the aromatic rings in the structure of bisphenol A, it ensures low volatility of the composition and a high modulus of cured composite. On the other hand triethyleneglycol dimethacrylate is an active diluent. In practice, mixtures of these monomers are used in a weight ratio of 7: 3 or 8: 2 where the main component is BisGMA [5-6].

Moreover, the commonly used photoinitiating system for the free-radical photopolymerization process is two component system based on camphorquinone and aromatic amine. In the step of generating radicals in the photolysis process, amine interacts with the excited camphorquinone molecule. This process involves the transfer of the electron from the amine to the ketone, followed by abstraction of the proton. The radicals, which initiate the polymerization process, are mainly formed from amines [7-11].

In this work, influence of different factors such as weight ratio of BisGMA and TEGDMA monomers, amine concentration, type of amine, type of diode on properties of standard dental light-cure composite resins were studied. The article also presents completely new, safe initiating systems intended for the production of a new generation of dental composites polymerizing via cationic mechanism, characterized by reduced polymerization shrinkage.

## METHODOLOGY

## 2.1. Materials

Bisphenol A-glycidyl methacrylate (BisGMA from Sigma Aldrich) and triethylene glycol dimethacrylate (TEGDMA from Sigma Aldrich) in the different ratio were applied as a model monomers for free-radical photopolymerization for dental application. Camphorquinone (CQ from Sigma Aldrich) and differens amines such as ethyl 4-(dimethylamino)benzoate (EDB from Sigma Aldrich), bis(hydroxyethyl)methylamine (MDA from Sigma Aldrich), 2-(phenylamino)acetic acid (NPG from Alfa Aesar ), triethanoloamine (ETA from Sigma Aldrich), triethylamine (ETA from Alfa Aesar) as photoinitiators systems were selected for the study.

3,4-epoxy cyclohexylmethyl 3,4-epoxycyclohexanecarboxylate (CADE, commercial name UVACURE® 1500, from Allnex) as model epoxy monomer and trimethylolpropane triacrylate (TMPTA, from Allnex) as an acrylate monomer in weight ratio 1:1 and novel photoinitiators – onium salt (0.5% w/w) were used in the production of innovative dental composites. Morover

the AEROSIL® R 9200 (from EVONIK) as the inorganic filler was selected for this study. In figure 1 structures of compounds used in this article were presented. All compositions of the studied compositions along with the calculated conversion rates are presented in Table 1 and Table 2.



Fig.1. Structures of compounds used in the article.

## 2.2. Methods and apparatus

To determine the conversion rate of monomers, the Real-time Fourier transform (real time-FT-IR) method was used. The equipment was composed of the Thermo Scientific i10 NicoletT<sup>M</sup> spectrometer with an appropriate horizontal adapter adjusted for real time measurements of photopolymerization processes of samples with a thickness of 1.4 mm. As the light source for photopolymerization measurements different diodes (from Thorlabs Inc.) were used. The light was emitted by the UV-LED diode to the sample with a liquid fiber optic cable (from Torlabs Inc.) with a diameter of 5 mm and a length of 1.2 meters was delivered. Measurements were recorded in the OMNIC program.

The photocurable formulations were deposited on a polypropylene (PP) films under air. The progress of photopolymerization process was monitored by observing the disappearance of the band at wave number equal approximately 6165 cm<sup>-1</sup> (Figure 2) for acrylate monomers and 3750 cm<sup>-1</sup> (Fig. 3) for epoxy monomer. The UV-LED diode was started 10 seconds after the start of spectral registration.



Fig.2. Near IR spectra recorded before and after polymerization for photoinitiang system camphorquinone (CQ)/ ethyl 4-(dimethylamino)benzoate (EDB) in a molar ratio of 1:3 photoinitiating system and bisphenol A-glycidyl methacrylate (BisGMA) and triethylene glycol dimethacrylate (TEGDMA) monomers followed at 6165 cm<sup>-1</sup>.



Fig.3. Near IR spectra recorded before and after polymerization for onium salt 12-078 (0.5 w/w) and 3,4-epoxy cyclohexylmethyl 3,4-epoxycyclohexanecarboxylate (CADE)/ trimethylolpropane triacrylate (TMPTA) monomers followed at 6165 and 3750 cm<sup>-1</sup>.

Because the decrease of absorption of the peak area is directly proportional to the number of polymerized groups, the degree of conversion of the function group was calculated by measuring the peak area at each time of the reaction by using equation 1:

$$C_{FT-IR} \left[\%\right] = \left(1 - \frac{A_{After}}{A_{Before}}\right) * 100\%$$
, (1)

where:

 $A_{Before}$  is an area of the absorbance peak characteristic for used monomer and type of photopolymerization before polymerization process and

A<sub>After</sub> is an area of the same absorbance peak, but after polymerization process.

#### RESULTS

In first step photoinduced free-radical polymerization of a standard monomers used in production dental composites in the presence of camphorochinone and ethyl 4- (dimethylamino)benzoate derivatives was investigated. In Figure 4 profiles for the composition composed of the camphorochinone and amine - ethyl 4-(dimethylamino)benzoate (in short EDB) in a molar ratio of 1 to 2 and different proportions of BisGMA/TEGDMA monomers are presented. The compositions were irradiated upon exposure to LED@455 nm. The incident light intensity at the sample surface was I<sub>0</sub>=18 mW·cm<sup>-2</sup>. The lowest conversion rate was obtained for the composition consist of BisGMA TEGDMA monomers in weight ratio of 8:2. On the other hand the photopolymerization of BisGMA TEGDMA monomers in weight ratio

of 7:3 was the fastest, because for this composition the greatest angle of kinetic curve and the shortest induction time were observed.

The next step the composition composed of the camphorochinone and various amounts of amine was studied. The lowest conversion rate was obtained for a composition consisted of camphorohinone and EDB in a molar ratio of 1-0.5. Amount of formed radicals was not enough for initiating this reaction what was connected with insufficient amount of amine. On the other hand, for compositions with an excess of amine in the molar ratio of camphorochinone : ethyl 4-(dimethylamino)benzoat 1: 2, even higher conversion rates were obtained (Figure 5).



Fig.4. Polymerization profiles (methacrylate function conversion) for bisphenol Aglycidyl methacrylate (BisGMA) and triethylene glycol dimethacrylate (TEGDMA) in different weight ratio and initiating system CQ/EDB in a molar ratio 1:2.





A variety of amines as co-initiators to camphorquinone can be used. Therefore, in the next stage, the influence of the type of amine on the photopolymerization process of standard monomers used in dentistry was studied. In Figure 6 the kinetic profiles for different initiating systems composed of CQ and different amines were presented. 5 amines were used: ethyl 4-(dimethylamino)benzoate (EDB), bis(hydroxyethyl)methylamine (MDA), 2-(phenylamino)acetic acid (NPG), triethanoloamine (TEA), triethylamine (TEtA). The highest degrees of conversion were obtained for the composition consisting of CQ and the amine EDB and CQ and NPG in a 1: 2 molar ratio. Nevertheless, the CQ / NPG system generates a strong yellow colour. By contrast, the system composed of tiertylamine or triethanolamine is cloudy. The most desirable amine used as a co-initiator is EDB amine as the greatest conversion is obtained. It has been proved that the type of amine influences not only the degree of conversion of acrylate monomers but also on the visual effect of the obtained filling, which is extremely important in stomatology.



Fig.6. Polymerization profiles (methacrylate function conversion) for bisphenol A-glycidyl methacrylate (BisGMA) and triethylene glycol dimethacrylate (TEGDMA) in a weight ratio of 7:3 and initiating system based on CQ (0.5% wt.) and different type of amines (1% wt.).

L.p.	Weight of CQ	Type of amine	Weight of CQ	Weight of ratio of BisGMA/TEGDMA monomers	Type of diode	Conversion [%]
			Diffrent rat	tio of monomers		
1	0.5% w/w	EDB	1% w/w	5:5	455nm	59.6
2				6:4		79.8
3				7:3		79.6
4				8:2		79.7
			Concentr	ation of amine		
5	0.5% w/w	EDB	0.5% w/w	7:3	455nm	68.6
6			1% w/w			72.5
7			2% w/w			76.3
8			3% w/w			76.6
Type of amine						
9	0.5% w/w	EDB	1% w/w	7:3	455nm	78.1
10		NPG				65.7
11		MDA				77.2
12		TEtA				72.6
13		TEA				67.7
Type of diode						
14	0.5% w/w	EDB	1% w/w	7:3	365nm	29.3
15					375nm	23.0
16					385nm	46.6

Table 1. The compositions of the tested compositions and the calculated conversion rates.

17			385nm	33.0
18			405nm	59.2
19			420nm	54.7
20			455nm	67.1
21			470nm	69.2
22			490nm	64.8
23			505nm	59.6
24			530nm	11.8
25			565nm	1.0

In the next step compositions composed of CQ / EDB in a 1: 2 molar ratio and BisGMA and TEGDMA monomers in a weight ratio of 7:3 were irradiated with different LEDs. In contrast, the incident light intensity at the sample surface was  $I_0 = 4 \text{ mW cm}^{-2}$ . The highest degrees of conversion were achieved when the compositions were irradiated with diodes at 455 nm and 477 nm, which corresponds to the highest extinction coefficients for camphorquinone (Figure 7). Therefore, modern dental lamps used in dentistry usually have built-in diodes with a maximum emission at a wavelength of 450 nm. I also showed that the content of silica in the standard light-curing composition with CQ /EDB as the initiating system and BisGMA / TEGDMA (in a weight ratio of 7: 3) has no effect on the final conversion rates. Furthermore, the silica content has been shown to influence the hardness of the dental composites: the higher the silica content, the greater the hardness (Figure 8 and Table 2).



Fig.7. Polymerization profiles (methacrylate function conversion) for bisphenol A-glycidyl methacrylate (BisGMA) and triethylene glycol dimethacrylate (TEGDMA) in a weight ratio of 7:3 and initiating system based on CQ (0.5% wt.) and EDB amine (1% wt.).

Fig.8. Dependence of Shora hardness on silica content in dental composites using the innovative initiating systems.

L.p.	Weight	Type of	Amine	Weight of ratio	of	Type of	Content	Shora
	of CQ	amine		BisGMA/TEGDMA		diode	of silica	hardness
				monomers				
1	0.5%	EDB	1% w/w	7:3		455nm	5% w/w	70
2	w/w						10% w/w	84
3							20% w/w	86
4							40% w/w	91
5							60% w/w	94
5							70% w/w	93

Table 2. The compositions of compositions consist of different amount of sillica and the Shora hardness.

Real-Time FT-IR measurements were also carried out for the composition consisting of 0.5 wt.% photoinitiator based on onium salt (12-078) and a mixture of CADE / TMPTA monomers in a weight ratio of 1: 1 with the addition of 40% silica AEROSIL® R 9200 (from EVONIK). As a reference, the composition without the addition of silica was used. The compositions were irradiated with a LED emitting radiation in the visible light range of 405 nm (24 mW/cm<sup>2</sup>). Figure 9 shows the dependence of conversion degrees for the two abovementioned compositions. Then it is clearly seen that the silica does not significantly affect the conversion rates from the acrylate monomer. Nevertheless, the arrangement with silica prevents the composite from producing the yellow colour which is desirable in dental composite (Photo 1).



Fig.9. Polymerization profiles for CADE/TMPTA in a weight ratio of 1:1 and initiating system based on onium salt 12-078 (0.5% wt.) with 40% silica AEROSIL® R 9200 and without 40% silica AEROSIL® R 9200.



0.5% 12-078 + CADE/TMPTA 0.5/0.5 + 40% AEROSIL

0.5% 12-078 + CADE/TMPTA 0.5/0.5

Photo 1. Photo showing composite of onium salt 12-078 (0.5% wt.) And mixture of monomers CADE / TMPTA (in weight ratio 1: 1) with 40% silica AEROSIL® R 9200 and without 40% silica AEROSIL® R 9200.

## CONCLUSIONS

Photopolymerization is an environmentally friendly method for obtaining new generation dental composites. The article shows that weight ratio of BisGMA and TEGDMA monomers, amine concentration, type of amine, type of diode has an effect on the conversion rates. The best composite consists of: CQ / EDB (in molar ratio 1: 2); BisGMA / TEGDMA (in weight ratio 7: 3) and a diode emitting radiation at a wavelength of 455nm.

Moreover the new composite consisting of onium salt 12-078 (0.5% wt.) and mixture of monomers CADE / TMPTA (in weight ratio 1: 1) with 40% silica AEROSIL® R 9200 was also developed. This composition is devoid of camforquinone and amines. Camforquinone produces a yellow colour, while amines can cause cytotoxic and genotoxic effects. Therefore, the composition presented by us can be an alternative to dental fillings used in dentistry, devoid of toxic amines and yellow colour.

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## PLASTIC IS FANTASTIC: FROM WASTEWATER TO BIOPLASTIC

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#### ABSTRACT

The urban domestic wastewater treatment plants (WWTPs) of the future are a net source of energy/valuable products, i.e., a water resource recovery facility (WRRF). While conventional WWTPs focus only on removing organic substrates and nutrients, WRRFs additionally aim to convert pollutants into valuable end products. One possibility is the conversion of organic carbon from wastewater into bioplastics. Polyhydroxybutyrates (PHBs) are macromolecules synthesized by bacteria. They are inclusion bodies accumulated as reserve materials when the bacteria grow under different stress conditions. Because of their fast degradability under natural environmental conditions, PHBs are selected as alternatives for biodegradable plastics production. This paper aims to isolate potential PHB producing bacteria from wastewater and evaluates PHB production using wastewater as carbon sources. The sample wastewater was from Vilnius WWTP, Lithuania. Among 50 isolates screened from the wastewater, 5 bacterial isolates were found to be the most promising PHB-producing bacteria. Screening for PHB was done by Sudan black and Nile blue A staining methods. PHB extraction was carried out by chloroform digestion method. 16s rRNA analysis showed that PHB-producing bacteria belong to Aeromonas. Isolates were grown in the wastewater of known composition. Quantitative evaluation of polymer isolated from Aeromonas media and Aeromonas sp. resulted in a high dry cell weight of 0.544 g/l and a reasonable polymer accumulation rate of 18% of Aeromonas media and dry cell weight of 0.080 g/l and a polymer accumulation rate of 4% of Aeromonas sp. PHB was characterized by FTIR spectroscopy.

Keywords: biomass, wastewater, bioplastic, PHB, Aeromonas, circular economy

## **INTRODUCTION**

In the last decade, urban domestic wastewater treatment plants have been intensively reconstructed in Lithuania, by installing nitrogen and phosphorus removal and sewage sludge treatment systems. After the reconstruction, some technologies, especially biological technologies did not work reliably. Many companies face difficulties improving biological technologies and sludge volumes are especially problematic. Unable to ensure the required degree of sludge treatment, the companies are forced to reduce the amount of generated sludge.

In recent decades, there has been a growing need to produce and use biodegradable polymeric material from biological (microbial, plant, etc.) and biomolecular sources such as polysaccharides, proteins, and lipids, which have been used as an inexpensive and renewable alternative to traditional polymers [1-2]. Thus, researchers are looking for the most suitable biodegradable polymers from various biological sources, including microorganisms. Fortunately, nature offers an alternative to petroleum-based polymers from natural biological resources [3].

Polyhydroxyalkanoates (PHAs) are biodegradable polyesters produced in bioprocesses from renewable resources compared to fossil non-biodegradable polymers [4]. PHAs are biologically synthesized and biodegradable polyesters with a wide range of thermal and mechanical properties [5]. PHB is a derivative of PHA that has been extensively studied and carefully described. They are similar to traditional petroleum plastics such as polyethylene and polypropylene [6]. Over the past few decades, this property has received a great deal of interest. PHB homopolymers can be easily manipulated due to their short chain ring flexibility and low crystallinity [6]. PHB polymers can also be produced and carbon sources, resulting in new biopolymers with exceptional properties. PHBs' production has been a significant obstacle to replacing traditional plastics with bioplastics, masking all its advantages due to high production costs [7].

More than 300 bacteria have been reported to possess biopolymer producers [3,8]. Among them, only a few numbers of bacterial cultures such as Azoto-bacter *Vinelandi i, E. coli, Pseudomonas oleovorans, Halomonas campaniensis, Alteromonas lipolytica, Aeromonas sp., Bacillus megaterium, Methylobacteria sp, Herbaspirillum seropedicae, Alcaligenes latus, etc. [3,10-11] are preferably used for PHB and PHA fabrication process. However, the commercialization possibilities of a bacterial-based biopolymer are less due to the production cost since using a purified form of nutritional factors like glucose, lactose, sucrose, etc. Henceforth, this research was framed to isolate PHB, producing predominant bacteria from the wastewater treatment plant and determining suitable growth conditions and cheap carbon and nitrogen sources for PHB fabrication by creating a circular economy.* 

#### **METHODS**

#### Sample area and collection

Wastewater samples were collected from Vilnius WWTP after the first radial precipitator. Vilnius WWTP wastewater was collected in 3×3 L glass containers previously cleaned by washing in non-ionic detergent, rinsed with tap water, and later soaked in 10% HNO<sub>3</sub> for 24 hours, and finally rinsed with deionized water before usage. The grab sampling was performed according to Standard Methods [12]. The samples were labelled and transported to the laboratory, stored in the refrigerator at about 4°C before analysis. Sample for PHB accumulating bacteria identification was collected in August 2020.

#### Isolation and preservation of bacterial strains

For isolation from the wastewater sample, 1ml of water sample was added in 99 ml sterilized water. After serial dilution  $(10^{-3} \text{ to } 10^{-7})$ , 0.1 ml of each dilution was spread on a carbon-rich nutrient agar plate and incubated at 37°C for 24 h [13-15].

Today, approximately 150 different hydroxy alkanoic acids are known to be incorporated into polyhydroxyalkanoates [16]. For the rapid detection and isolation of PHB producing bacteria, 0.02% alcoholic solution of Sudan black B (ROTH) was applied to stain bacterial colonies, and the plates were kept undisturbed for 30 min. The excess dye was then decanted, and plates were rinsed gently by adding 96% ethanol.

## Screening for PHB producing bacteria

Sudan black B positive isolates were checked for PHA production by Nile blue A (ROTH) staining, a more specific stain for PHAs by a more rapid and sensitive, viable colony method [17]. This dye at concentrations of only 5  $\mu$ l/ml was directly included in carbon-rich nutrient agar medium (beef extract 10, peptone 10, sodium chloride 5, and agar 18), and growth

of the cells occurred in the presence of the dye [18]. Plates were incubated at 37°C for 24 h [15]. Nile blue A staining showed bright orange fluorescence on irradiation with UV light, and their fluorescence intensity increased with the increase in PHA content of the bacterial cells. The isolates which showed bright orange fluorescence on irradiation with UV light after Nile blue A staining were selected as PHA accumulators [14].

E. coli DH52 and S. cerevisiae AH22 were used as control group cultures.

#### **Identification of PHB producing isolates**

For bacterial genomic DNA isolation, amplification, purification, and 16S rDNA gene sequencing, the bacteria were plated on microbiological medium (peptone; beef extract; NaCl; agar) Petri dish and submitted to the Molecular Ecology Laboratory of the Center for Natural Research for analysis. DNA sequencing reactions were prepared using the BigDye Terminator v3.1 Cycle Sequencing Kit. The analysis was performed on an automated 16-capillary genetic analyser 3130×1 Applied Biosystems, which performs electrophoresis, laser detection, and computer analysis of fluorescently labelled DNA fragments.

The sequenced sequence was compared to the 16S rDNA sequences in the NCBI database using the BLAST computer program.

## **Pretreatment of wastewater**

Vilnius city municipal wastewater after the first radial precipitator (3 l) was examined according to international and national standards (Table 1). Measured parameters – suspended solids (SS), chemical oxygen demand (COD), biological oxygen demand (BOD<sub>7</sub>), total phosphorus (Total P), total nitrogen (Total N), NH<sub>4</sub>-N, PO<sub>4</sub>-P, and lipids. 2 l of the medium was autoclaved for 15 min at 1 atm. at 121 °C.

Measured parameters	Reference
SS mg/l	LAND 46-2007
COD mg/l	ISO 15705:2002(E)
BOD <sub>7</sub> mg/l	LAND 47-1:2007
Total P mg/l	LAND 58:2003
Total N mg/l	LAND 84:2006, LAND 59:2003
NH <sub>4</sub> -N mg/l	LAND 38:2000
PO <sub>4</sub> -P mg/l	LAND 58:2003
Lipids, mg/l	SVP-17

Table 1. Standard municipal wastewater indicators

## Production of PHB by selected isolates

Seed culture media was prepared containing g/l;  $Na_2HPO_4$  6.36,  $KH_2PO_4$  2.7,  $(NH_4)_2SO_4$  4.70,  $MgSO_4$  0.39, glucose and trace element solution 1 ml/l was added. pH was kept at 7.0 for the growth of isolates. The inoculum was prepared in 50 ml flasks and incubated at 37°C for 24 h at 150 rpm [15].

After growing, the cells are centrifuged at 5 000 rpm for 10 min. After centrifugation, the supernatant is discarded and the cells are transferred to 250 ml of autoclaved effluent of known composition.

#### **Extraction and quantification of PHB**

Together with 10 ml of 12% sodium hypochlorite, the biomass is incubated at 50°C for 1 hour to lyse the cells. The resulting cell extract was centrifuged at 12 000 rpm for 30 minutes, followed by successive washing with distilled water, acetone, and absolute ethanol. After washing, the residual biomass was dissolved in 10 ml of chloroform (99%), incubated overnight at 50°C, and then evaporated at room temperature. Quantitative analysis was performed.

For quantitative analysis of PHA, cell culture was grown as described earlier and cell pellet was dried to estimate the dry cell weight (DCW) in units of g/l [19]. Residual biomass was estimated as the difference between dry cell weight and dry weight of extracted PHA [20].

This was calculated to determine the cellular weight and accumulation other than PHAs.

The percentage of intracellular PHA accumulation is estimated as the percentage composition of PHA present in the dry cell weight [14]:

Residual biomass 
$$\left(\frac{g}{l}\right) = DCW\left(\frac{g}{l}\right) - Dry$$
 weight of extracted PHA  $\left(\frac{g}{l}\right)$ , (1)

 $PHA accumulation (\%) = Dry weight of extracted PHA <math>\left(\frac{g}{l}\right) \times \frac{100\%}{DCW} \left(\frac{g}{l}\right).$  (2)

#### FTIR spectrophotometer analysis of PHB

Polymer identification was performed with a Bruker Alpha FT-IR spectrometer equipped with an ALPHA Platinum ATR single-reflection diamond ATR module (Center for Physical Sciences and Technology, Vilnius). In FT-IR spectroscopy analysis, during the contact between radiation and a polymeric material, waves of some frequencies are absorbed and others are transmitted through the absorption of radiation, the bonds begin to vibrate, and the totality of those oscillations is the IR spectrum. Different compounds of the compound absorb IR radiation of different wavelengths, and thus the molecular composition of the polymer is determined from the absorption spectra obtained. Spectrum recording was performed in the range of 4 000-400 cm<sup>-1</sup>, 24 scans, resolution 4 cm<sup>-1</sup>.

## **RESULTS AND DISCUSSION**

## **Identification of polymer aggregates**

After incubation,  $10^{-2}$  to  $10^{-3}$  dilution Petri dishes were selected for bacterial passage (Fig. 1). To determine that the available bacterial culture cells accumulate polymers, 50 single colonies were inoculated into the microbiological medium in a Petri dish and incubated for 24 hours at 37°C. The resulting preparations were stained with a 0.02% solution of Sudan black B alcohol, and the Petri dishes were left immobilized for 30 min. The excess dye is then decanted, and the plates are gently washed with 96% ethanol solution. Bacterial colonies that cannot absorb Sudan's black B solution remain white, and PHB producers are bluish-black [13-14].



Fig. 1. Sudan black B-affected colonies, dilution 1000 times (left), 100 times (right)

The ability of the isolates to synthesize PHA is checked by selective Nile blue A azo dyes; this dye, at a concentration of only 5  $\mu$ l/ml, is added directly to a medium rich in carbon (peptone; beef extract; NaCl) and the cells were grown in the medium in the presence of a dye-plate and incubated at 37°C for 24 hours.

Nile blue A azo dye elicited bright orange fluorescence upon irradiation of colonies with PHA. The intensity of the luminosity increases with increasing PHA content in the bacterial cells. The results of the use of Nile blue A azo dye are presented in Fig. 2.



Fig. 2. Results of application of Nile blue A azo dye when diluted 1 000 times (left) and 100 times (right)

The following strains were selected for further research:

- Right (diluted 1 000): 43, 46. 22 were sent for examination due to an unusual color glow.
- Left (diluted 100): 14, 20, 37.

*E. coli* DH52 and *S. cerevisiae* AH22 grown under identical conditions. *E. coli* DH52 used as a control did not show a response to azo dye, and *S. cerevisiae* AH22 induced bright orange fluorescence but did not grow at all on the selective medium. For bacterial genomic DNA isolation, amplification, purification, and 16S rDNA gene sequencing, the bacteria were

plated on microbiological medium (peptone; beef extract; NaCl; agar) in a Petri dish and submitted to the Molecular Ecology Laboratory of the Center for Natural Research (Vilnius) for analysis.

## Sequencing of the 16S rDNA gene

Sequencing of the 16S rDNA gene was performed to determine the type of bacterium under study. The sequenced sequences were compared to the 16S rDNA sequences in the NCBI database using the BLAST computer program. The results of the BLAST program comparison and the identified genera are shown in Table 2.

Isolate no.	A genus has been identified	Similarity to species
46	Proteus	Proteus mirabilis
43	Brachymonas	Brachymonas denitrificans 98.35 %
14	Aeromonas sp.	Aeromonas media
20	Aeromonas sp.	A. hydrophilia, A. caviae, A. enteropelogenes, A. taiwanensis, A. sanarellii
37	Enterobacterales	Enterobacter, Leclercia, Klebsiella, Pantoea – 99 %
22	Pseudomonas	Pseudomonas aeruginosa

 Table 2. BLAST program comparison results

## Polymer synthesis, isolation, purification and transfer to wastewater

For further studies, only *Aeromonas sp.* isolates were used. The prepared liquid mineral salt medium was used to grow the isolates. The pH maintained for the growth of the isolates was 7.0. The inoculum was prepared in 50 ml flasks and incubated at 37°C for 24 hours at 150 rpm.

After seeding, the cells were centrifuged at 5 000 rpm for 10 min. After centrifugation, the supernatant was discarded and the cells were transferred to 250 ml of autoclaved effluent of known composition (Table 3).

Measured parameters	After the first precipitator	After autoclaving	Variation (%)
SS mg/l	SS mg/l 108		+114.81
COD mg/l	449	1004	+123.61
BOD <sub>7</sub> mg/l	202	615	+204.46
Total P mg/l	9.03	8.62	-4.54
Total N mg/l	64	45	-29.69
NH4-N mg/l	60	34	-43.33
PO <sub>4</sub> -P mg/l	7.36	4.69	-36.28
Lipids mg/l	36	25	-30.56

 Table 3. Changes in wastewater parameters after autoclaving

Part of the lipids were broken down and switched to COD, COD increased due to the appearance of protein denaturation products. More research is needed to determine why the amount of nitrogen and phosphorus and their compounds in wastewater vary when exposed to high temperatures. It is suggested to evaluate the number of carbohydrates in wastewater and how their content changes under the influence of temperature as research continues.

After lysis of the cells, the resulting polymers were washed and extracted with hot chloroform, and the chloroform was evaporated. A typical polymer view is shown in Figure 3.



Fig. 3. The polymers were obtained after separation and purification, here: from left: 14 – *Aeromonas sp.*; 20 - *Aeromonas sp.* 

The polymer mass and the total yield from the dry cell mass are determined. The results obtained after polymer isolation and purification are shown in Table 4.

A genus	DCW (g/l)	Weight of extracted and dry polymer (g/l)	Residual biomass	Polymer accumulation (%)
20 - Aeromonas sp.	2.944	0.544	2.400	18.478
14 - Aeromonas sp.	0.210	0.008	0.202	3.810

Table 4. Quantitative evaluation of polymers released from the effluent

*Aeromonas sp.* shows a possible polymer accumulation from 3.810% to 18.478%. The data obtained suggest that more detailed genetic testing is needed.

## Identification of polymers by ATR-FTIR spectroscopy

FT-IR analysis of polymers isolated from bacterial cultures was performed to identify the PHB polymer and identify functional groups (Fig.4 and Fig. 5).



Fig. 4. 20 - Aeromonas sp. polymer spectrum



Fig. 5. 14 - Aeromonas sp. polymer spectrum

*Aeromonas sp.* synthesizes not a PHB but a copolymer. For example, PHA synthase from *Aeromonas caviae* is able to synthesize P(3HB-co-3HHx) because it has a high an affinity for both 3HB and 3HHx units, unlike other PHA synthases that show affinity for only 3HB unit [21].

The absorption peaks are at the methyl and methylene groups, which show the C-H bond's deformation oscillations. At 1723-1671 cm<sup>-1</sup> is characteristic of valence oscillations of ester functional groups. At the peak of 1456 cm<sup>-1</sup>, it belongs to the -CH group. Spectral peaks from 1200 to 900 wavenumbers correspond to C-O-C oscillations. Summarizing these FT-IR results and comparing them with the spectrum of a standard PHB, it can be stated that the polymer under study is a copolymer P (3HB-co-3HHx) with the structural formula:



*Aeromonas* genera members have shown some advantages in the production of polyhydroxyalkanoates, especially scl-mcl-PHAs copolymers. Due to their vigorous growth and simple substrate needs, these bacteria become potential industrial biopolester production hosts [21]. P(3HB-3HHx) was produced on a large scale by *Aeromonas hydrophila* at Tsinghua University (China) in collaboration with Guangdong Jiangmen Biotechnology Development Center (China), KAIST (Korea), and Procter & Gamble (USA) to develop a fermentation strategy in a 20 000 l bioreactor [22].

The extracted and purified biopolymer has been used to make nonwovens, binders, flexible packaging, thermoformed products, synthetic paper, and medical devices [22].

#### CONCLUSION

This study confirmed that cheaply available wastewater after simple biological treatment could be used to produce PHBs. Using wastewater to produce PHBs will reduce the cost of biodegradable plastics and improve the environmental pollution caused by conventional plastics. It will also solve the disposal problems at the wastewater facilities by increasing sludge volumes.

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# THE CHANGES IN DEOXYNIVALENOL CONCENTRATION AND NUTRITIVE COMPOSITION IN MAIZE GRAINS DUE DELAYING HARVESTING

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#### ABSTRACT

The scientific literature emphasizes that grain is the most valuable part of maize, although biomass of the whole plant is most often used as feed. Maize does not always manage to ripen grains in cool climate zones, but there are already more and more hybrids on the market that are suitable to mature grains in Lithuania. There is a lack of information on the maize grains contamination with mycotoxin deoxynivalenol (DON) in fields and during cob maturation, when they are grown in Lithuania. The aim of this study was to investigate whether maize grain harvest time and different maize hybrids affect the concentration of this mycotoxin and maize nutrient composition. Two maize hybrids for grains were sown: Lapriora (FAO 190) and Duxxbury (FAO 170) in experimental fields in 2020. Cobs with grains were first harvested at physiological maturity (BBCH 87). The other two harvests were implemented 10 and 21 days after physiological maturity. DON analyses were performed by high performance liquid chromatography. Nutritive composition was determined using ground chemical methods. The obtained results were processed by IBM SPSS Statistics 25 program. The study has shown that all samples of maize grains were contaminated with DON. The levels of DON in grains were found low, but a delay in harvest revealed an increase in DON concentration. There were some significant differences (P<0.05) in DON concentrations between the two maize hybrids. The biggest and statistically significant differences (P<0.05) were found between the first and third harvest results. Only few statistically significant (P<0.05) changes were noticed in nutritive composition: both maize hybrids DM and starch content increased and Fe concentration decreased.

Keywords: mycotoxins, feed, harvest time, nutrition, maize hybrids

#### INTRODUCTION

Maize grain mainly has been used for farm animal feed and secondarily for human food and biomass [1]. Maize is enriched with macronutrients like protein (~10%), fat (~4%), starch (~72%) and fiber and with micronutrients like  $\beta$ -carotene, vitamin B complex and minerals like magnesium, phosphorus, zinc, copper, etc. [2, 3]. Therefore, maize is one of the most important crops for livestock feed and human nutrition [4]. From 1990 till 2020 United States of America have increased their maize production more than 1.8 times and maize takes first place among other grains in USA. In 2020 maize production reached 360252 thousand tons in this country and this stands for 31.77% of the world's maize production [5]. Maize production increased 3 times in the last 10 years in Lithuania and in 2020 it was 143 thousand tons [6].

Unfortunately, maize is often infected by *Fusarium* fungi. *Fusarium* species that cause ear and stalk rot, such as *F. graminearum*, *F. verticillioides* and *F. subglutinans*, also produce numerous mycotoxins, among which, one of the most important is deoxynivalenol (DON) [7]. DON toxicosis causes weight loss for animals, reduces feed intake, triggers pro-inflammatory and immunological responses and a high concentration in feed causes vomiting [8, 9, 10]. Therefore, Europe Commission Recommendation for mycotoxins in grains for animal feed sets recommended DON level to less than 8000  $\mu$ g kg<sup>-1</sup> and Europe Commission Regulation sets maximum levels for DON in foodstuffs: for unprocessed maize grains 1750  $\mu$ g kg<sup>-1</sup>, for cereals intended for direct consumption 750  $\mu$ g kg<sup>-1</sup>, for baby food, infants, young children 200  $\mu$ g kg<sup>-1</sup> [11, 12]. However, ongoing research is needed to ensure safety in the maize-based food and feed chain [13].

Meteorological conditions are very important for DON production. Frequent rainfalls and low temperatures increase maize contamination with *Fusarium* fungi and result in contamination with DON [14]. The choice of certain maize hybrids could also result in a variable selection of the fungal species that can infect and develop on maize ears and this could result contamination with mycotoxins produced by those fungal species [15]. There is a lack of information about DON concentration changes in maize grains and their hybrids by delaying harvest time, however there are researches that try to answer this question by exploring different grains [16, 17].

Maize grain nutritive value also can change because of delayed harvest time. Some other researchers have noticed changes by delaying harvest time, but there is still a paucity of information about mineral content changes [18, 19, 20]. Therefore, further research is needed to identify future risks that may increase mycotoxin contamination and decrease quality of maize [13].

The aim of this study was to investigate whether maize grain harvest time and different maize hybrids affect the concentration of DON mycotoxin in maize and maize nutrient composition.

## MATERIALS AND METHODS

#### Samples

Two maize hybrids with different FAO number were investigated: *Duxxbury (FAO 170)* and *Lapriora (FAO 190)*. A total of 24 maize grain samples (about 1kg per sample) were collected during autumn in 2020 at the experimental site of Institute of Agriculture, Lithuanian Research Centre for Agriculture and Forestry. Samples were collected from four randomized replication plots in three stages: at physiological maturity (when grain has a black dot at the point of attachment and about 60% of dry matter BBCH 87), then 10 and 21 days after first harvesting time. The samples were stored in the freezer at  $-18^{\circ}$ C until analyses.

#### **Mycotoxin analyses**

#### **Instruments**

DON mycotoxin and its concentration were determined with high performance liquid chromatography (HPLC) Shimadzu prominence consisting of LC-20 AT pump equipped with FCV-10AL quaternary valve, DCU-20A5 degasser, SIL-20A autosampler, CTO-20A column oven, ultraviolet detector; wavelength of 218 nm, equipped with chromatography column YMC – Pack Pro C18/S-3  $\mu$ m/12 mm size 150x4.0 mm (Japan). Items used for sample preparation: analytical balances with 10<sup>-3</sup> g accuracy from Explorer Ohaus (Germany), laboratory mill RETSCH<sup>®</sup> ZM200 (Germany), shakers - Reax Coniro Heidolph and HS501 digital IKA<sup>®</sup> - WERKE (Germany), rotary evaporator IKA RV 06-ML 2-B with adjustable vacuum system, filter papers Frisenete No. 204F (pore size 12-15  $\mu$ m) and Frisenete No. GC (pore size 1.2  $\mu$ m), immunoaffinity columns – NeoColumn for Deoxynivalenol (DON) NEOGEN Europe<sup>Ltd</sup> (Germany), laboratory glassware and micropipetts (20-200, 1000-5000 and 5000-10000  $\mu$ ]).

#### Reagents

Reagents used for sample preparation and DON determination: acetonitrile CH<sub>3</sub>CN for HPLC from VWR International (France), methanol CH<sub>3</sub>OH for HPLC from PANREAC QUIMICA (Spain), polyethylene glycol 8000 from AppliChem (Germany), crystalline deoxynivalenol standard from AppliChem (Germany), deionized water (18.2 m $\Omega$ cm<sup>-1</sup>) made with water cleaning system Milipore (USA). Maize reference sample was purchased from Trilogy Analytical Laboratory (Washington, MO, USA).

#### Sample preparation

Grain samples were prepared and analysed according to European Standard (EN 15891: 2010: E). All samples were grounded into flour and 25 g  $\pm$  0.001 g of each sample were weighed and mixed with 5 g  $\pm$  0.001 g polyethylene glycol and 200 ml of deionized water. Samples were stirred with a shaker for 2 hours, then filtered through corrugated filter and glass filter. Two ml of the final extract was placed into the DON test column. For column washing 5 ml of deionized water was used. The elution of DON was done by 2ml CH<sub>3</sub>OH. The elution solvent was evaporated to dryness (at 50°C) and dissolved with 1 ml mobile phase (H<sub>2</sub>O:C<sub>2</sub>H<sub>3</sub>N:C<sub>2</sub>H<sub>4</sub>O<sub>2</sub> 90:10:0.1).

#### Method validation

The five-point calibration curve was made in the concentration ranges  $2-40 \ \mu g \ ml^{-1}$  for DON. Each standard solution was injected into chromatographic column three times and the working range was established.

Limit of detection (LOD) and limit of quantification (LOQ) were calculated on the basis of signal-to-noise ratio. For LOD it was 3 and for LOQ 10. Different concentration (1000 and 2000  $\mu$ g kg<sup>-1</sup>) of fortified samples were used to determine repeatability. Analyses were performed in different days. LOD, LOQ, recovery (%), relative standard deviation (RSD, %), correlation coefficient (R) was then calculated.

#### Nutrient composition analyses

Samples were grounded to mill and delivered to chemistry research laboratory for nutrient composition analyses. To determine dry matter (DM, %) content, the sample was dried at  $105^{\circ}$ C temperature until the weight was stable. Crude protein (CP, %) content was measured by the Kjeldahl method (ISO 5983-1:2005, Animal feeding stuffs – Determination of nitrogen content and calculation of crude protein content -Part 1: Kjeldahl method). The crude ash (CA, %) content of maize grain was determined by the gravimetric method. Starch (%) content was determined by the polarimetric method after hydrolysis of starch and other saccharides in hydrolic acid solution and after precipitation of protein substances (ISO 10520:2000, Native starch. Determination of starch content. Ewers polarimetric method). Minerals were determined by spectrophotometry (Varian Cary50) and atom absorptiometry (Perkin Elmer, AAnalyst 200) [21, 22].

## Statistical analysis

Mean values, standard errors and significance of data were calculated using IBM SPSS Statistics 25 software. One-way analysis of variance (ANOVA) was used to determine statistically significant differences between the DON concentration means. Means were compared using the Duncan's criterion. For samples, which concentrations did not exceed LOD, zero was used instead. The differences were significant with a confidence level of P<0.05.

#### **RESULTS AND DISCUSSION**

Method validation showed these results: according to the linear regression analysis, the calibration curve for DON was linear from 2 to 40  $\mu$ g ml<sup>-1</sup>, corelation coefficient (R) of calibration curve was 0.9998, retention time was 10.5 minutes, LOD was 46  $\mu$ g kg<sup>-1</sup>, mean recovery was 99 + 3%. These results indicate that chosen analytical method showed good accuracy for the detection of DON.

All tested samples of maize grains were contaminated with DON. The concentrations found were low, but a delay in harvest revealed an increase in DON concentration. Comparing all samples by harvesting time, it was noticed that DON concentrations got significantly higher (P<0.05) with each harvest: 1<sup>st</sup> harvest – 174 ± 7.2  $\mu$ g kg<sup>-1</sup>, 2<sup>nd</sup> harvest – 216 ± 5.4  $\mu$ g kg<sup>-1</sup>, 3<sup>rd</sup> harvest – 253 ± 11.5  $\mu$ g kg<sup>-1</sup> (Fig. 1).



*Notes.* Error bars show standard error. Different letters a-c show statistically significant differences between means (P<0.05).

#### Fig. 1. DON concentration in all samples by delaying harvest time

There were statistically significant differences (P<0.05) noticed between DON concentrations in maize hybrids by delaying harvesting time. DON concentrations in first two Lapriora hybrid harvests had significant differences with third harvest DON concentration:  $1^{st}$  harvest –  $198 \pm 8.7 \ \mu g \ kg^{-1}$ ,  $2^{nd}$  harvest –  $229 \pm 7.8 \ \mu g \ kg^{-1}$ ,  $3^{rd}$  harvest –  $273 \pm 19.8 \ \mu g \ kg^{-1}$ . Duxxbury hybrid DON concentrations had significant differences between all harvest times:  $1^{st}$  harvest –  $150 \pm 7.7 \ \mu g \ kg^{-1}$ ,  $2^{nd}$  harvest –  $202 \pm 5.9 \ \mu g \ kg^{-1}$ ,  $3^{rd}$  harvest –  $233 \pm 10.2 \ \mu g \ kg^{-1}$  (Fig. 2). There is a paucity of information about DON concentration changes in maize grains, but other researchers exploring different cereals have also noticed an increase of DON concentrations by delaying harvesting time. In England, 1 month delay in harvest resulted in a 10 times greater mean of DON concentration in wheat [17]. In Lithuania at 2017 DON concentration in spring oats increased almost by 2 times and in spring triticale by 3.5 times delaying harvesting time [16]. Only fumonisin levels were analysed in three maize hybrids in Brazil and it was found that fumonisin levels in maize grains significantly increase by delaying harvest time [23].



*Notes.* Error bars show standard error. Different letters a-c show statistically significant differences in maize hybrid (P<0.05).

## Fig. 2. DON concentration in different hybrids by delaying harvest time

Significant differences were also found between DON concentrations comparing maize hybrids at  $1^{st}$  and  $3^{rd}$  harvest, but there were no significant differences between hybrids at  $2^{nd}$  harvest. In all cases Lapriora was more contaminated than Duxxbury. However, delay in harvesting impacted more on Duxxbury than Lapriora, resulting in DON content increasing by 17% more in Duxxbury grains harvested later. (Fig. 3). Earlier research in Poland established that different hybrids of maize cobs are infected with *Fusarium* fungi and mycotoxins at various levels [24]. Research in North-West-Italy have showed different maize hybrids susceptibility: one of the hybrids (DKC6815) had the highest contamination level for all mycotoxins and metabolites [15]. Research in Brazil also showed significant differences in mycotoxin concentrations between maize hybrids [23]. Therefore, the choice of maize hybrid can lead to a higher mycotoxin contamination [15].





Fig. 3. DON concentration increase (%) in different hybrids by delaying harvest time

The harvesting time did not significantly (P>0.05) influence the nutrient composition in hybrids. Only few significant differences were noticed: in Lapriora hybrid where DM and starch increased by 1.3 % and 1.9 %, respectively and in Duxxbury hybrid where DM, CA and starch increased by 1.8%, 0.2 % and 1.2 %, respectively (Table 1). Seleiman (2017) states that as the plant matures, DM content and starch content usually increase, while crude ash (CA) and CP decrease [18]. The same result was obtained in Italy by Salama [19]. However, in our study CP and CA did not change at all or increased very slightly.

		1st harvest (BBCH 87)	2nd harvest (+10 days)	3rd harvest (+21 days)
	DM, %	$87.6 \pm 0.2$ a	$87.6 \pm 0.2$ a	$88.9 \pm 0.1$ b
Louisono	CP, % in DM	$7.9 \pm 0.2$ a	$8.1 \pm 0.3 a$	$8.6 \pm 0.2 \ a$
Lapriora	CA, % in DM	$1.33 \pm 0.07$ a	$1.35 \pm 0.09$ a	$1.45 \pm 0.02 \text{ a}$
	Starch, % in DM	$72.6 \pm 0.1$ a	$73.2 \pm 0.2$ a	$74.5\pm0.4~\textbf{b}$
	DM, %	$87.2 \pm 0.4 \text{ a}$	$87.6 \pm 0.1 a$	$89 \pm 0.2$ b
Duvyhury	CP, % in DM	$7.5 \pm 0.1 \ a$	$7.6 \pm 0.2 \text{ a}$	$7.9 \pm 0.1$ a
Duxxbury	CA, % in DM	$1.34 \pm 0.07$ a	$1.39 \pm 0.01$ a	$1.54\pm0.04~\textbf{b}$
	Starch, % in DM	$73.4 \pm 0.3$ a	$74.4\pm0.4~{\bm b}$	$74.6 \pm 0.1$ <b>b</b>

Table 1. Nutrient composition changes in hybrids by delaying harvest time

*Notes.* DM – dry matter, CP – crude protein, CA – crude ash. Different letters a-b show statistically significant changes in nutrient value between harvest times (P < 0.05).

The trend was noted that delay in harvesting resulted in decreasing of mineral concentration in maize grains. Although the reduction of P, Ca, Mg and Zn content in maize was not significant (P>0.05), the level of Fe diminished significantly (P<0.05). The concentration decreased by 31% (Fig. 4). There is a lack of information about mineral concentration changes in maize grains by delaying harvest time. The study of impact of delay in harvesting on mineral content (C, N, K, Ca, Na, Mg) in maize grains done by other researchers determined only significant reduction in K and Na, while other mineral concentrations diminished insignificantly [20].



*Note.* Different letters a-b show statistically significant changes in mineral concentration between harvest times (P < 0.05).

Fig. 4. P, Ca, Mg (A - % DM) and Zn, Fe (B  $-mg kg^{-1}$ ) concentration changes by delaying harvest time

#### CONCLUSIONS

Our research detected that DON contamination in maize grains can significantly (P<0.05) increase due to delayed harvest. The same tendency was observed when examining maize hybrids separately. The highest DON concentrations were found in Lapriora hybrid, however,

the increase in DON contamination with delayed harvest was more noticeable in Duxxbury hybrid. Nutritive composition remained almost the same and only few statistically significant changes were noticed: in both maize hybrids DM and starch content have increased and Fe concentration have decreased. Further research is needed to identify future risks that may increase mycotoxin contamination in maize.

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# ECO-FRIENDLY DYEING: AN APPROACH TOWARDS THE CHEMICAL FREE TEXTILES

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#### ABSTRACT

In recent years increasing frequency of pollution is leading toxicity in the environment. In this regard, the most significant category is synthetic organic chemicals produced by industries. The textile industry uses an average six hundred dyes and chemicals for the production of consumer's fabric material causing environmental pollution of various categories. A wide variety of colour producing synthetic dyes also release toxic wastes hazardous to all organisms. In the dyeing process, a fixing agent (mordant) is required to attach dyes to the fabric. Such type of all the mordants are heavy metals that extremely toxic, and bad for the environment, as well. To move in the direction of zero pollution, natural dyes and mordants could be the best option against hazardous chemicals. In the present investigation two natural dyes Eucalyptus globulus, Butea monosperma were applied on cotton fabric. Punica granatum and Musa sp. used as biomordant. The dyed fabrics were accessed through colourfastness properties against washing, light, and rubbing. Colourfastness of dyed samples ranged from good to excellent. Hereafter physicochemical characteristics of the natural and chemical dyeing effluent samples were evaluated to determine the difference. The results revealed that effluent originated by chemical dyes elevated pollution of water bodies. Whereas effluent originated by natural dyes are less polluting.

Keywords: Pollution, natural dye, mordant, chemical dyes, effluents

#### **INTRODUCTION**

Textile industries positively affect the economic development worldwide. China is on top in the list of exporter country of all types of textiles, then European Union, India and USA [1]. In textile industries scouring, bleaching, mordanting, dyeing and washing consumes lots of water. These large amounts of waste water discarded in soil or water bodies by industries. Textile effluents consist of several synthetic dyes and toxic chemicals containing acids, sulphur, alkalis, naphthol, nitrates, hydrogen peroxide, surfactant-dispersing agents and toxic heavy metals such as cadmium (Cd), lead (Pb), zinc (Zn), nickel (Ni), copper (Cu) and chromium, which are directly discharged into water streams [2]. These effluents are highly concentrated in dyes and chemicals, Some of these are non-biodegradable and carcinogenic. It increases chances of bio accumulation and biomagnifications in aquatic plants, animals and human being. These dyes and chemicals, in addition to their unacceptable appearance and toxic effect after their breakdown, may contaminate the nearby soil, sediment, surface water and become a major global environmental pollution challenge. Dyes in a water source can cause some disease ie. ulceration of skin, haemorrhage, skin irritation and dermatitis [3]. They block the penetration of sunlight from water surface to prevent photosynthesis. Discharged effluent by the industries is one of the sources of pollution. Contaminated air, soil, and water by industrial effluents are associated with heavy disease burden. These chemicals are not only poisonous to humans but also found toxic to aquatic life [4]. This could be part of the reasons for the current shorter life expectancy in the country, compared to the developed nations [5].

Environmental pollution is not new to us. It is a biggest problem facing by all over the world. European commission has been launched the "zero pollution plan" on 11 November 2020. It intends to better prevent, remedy, monitor and report on pollution. In 2021, the European Commission will adopt the action plan "Towards a Zero Pollution Ambition for air, water and soil – building a Healthier Planet for Healthier People"[6].

Natural dyes are derived from natural resources such as plant, animal, mineral, and microorganism [7,8]. Among these plants are the major sources of natural dyes [8]. Mordants are auxiliary dyeing substances that can form complexes with molecules of dyes [9]. Before the discovery of the first synthetic dye in 1856, all the colourant used for the colouration of textiles were of natural origin [10]. The use of natural dyes declined tremendously because of existing natural dyes failed to full fill the demand of the market [11]. However, these synthetic dyes have a adverse impact on human health and the environment. Therefore, in present study an attempt was made to dye fabrics naturally and avoid hazardous chemicals in dyeing process. Two natural dyes *Eucalyptus globulus, Butea monosperma* were applied on cotton fabric. *Punica granatum* and *Musa* sp. used as biomordants. The dyed fabrics were accessed through colourfastness properties against washing, light, and rubbing. Physicochemical characteristics of effluent generated by the natural and chemical dyeing were evaluated to determine the difference.

#### **MATERIALS AND METHODS**

#### Natural dyes collection:

Flowers of *Butea monosperma* and *Eucalyptus globulus* leaves were collected from Alirajpur, Dhar road and Holkar science college campus Madhya Pradesh (M.P) respectively. Flowers and leaves were dried at room temperature then crushed in grinder and stored in airtight containers.

#### Natural dyes collection:

The collection of *Musa sp.* (Banana) pseudostem sap was done from field of Raver Tehsil just near Burhanpur and Kasrawad (M.P.). After harvesting banana the whole plant becomes useless, its pseudostem cut and dumped as a waste. The pseudostem taken and cut in pieces then liquid collected with the help of juice machine. After that sap stored in glass bottles in refrigerator for further analysis. *Punica granatum* (Pomegranate) was purchased from local market of Indore. Pomegranate rind peeled out from fruits and dried on room temperature. Dried rinds grounded in mixer to prepare powder and stored in airtight container.

All the dyes and mordants stored for further experimentation.

## Fabric collection:

Handloom cotton (Khadi) was purchased from Khadi Bhandar (Indore Khadi Sangh) Rajwada Indore (Madhya Pradesh), India.

#### **Dye extraction:**

Dried powders of dyes were taken for the preparation of aqueous extraction of dye. Fifteen grams of dye powder (15% oven weight of fabric) weighed and poured in a beaker and soaked in 100 ml water for 15 minutes at room temperature. Dye pot (beaker) kept on high temperature (95-100° C) till boiling then extracted for one hour at 60°C. The extraction liquor was then filtered to obtain aqueous solution of dye [12]. The temperature and time of extraction selected on the basis of reviewed literature and experimentation.

## **Dyeing:**

Dyeing of fabric was performed under optimized conditions acquired through experiments. Fabric dyeing depends on concentration of mordants, pH, temperature and time. 15% concentration of dye was applied with both mordants. The dyed material was washed with cold water and dried at room temperature. Combinations of dyes and mordants that were prepared for the dyeing process are presented in Table 1.

S.No	Dyes and mordant combination
1	Eucalyptus+Musa sp.
2	Eucalyptus +Punica granatum
3	Butea+Musa sp.
4	Butea+ Punica granatum

Table 1. Dyes and mordant combination
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#### **Fastness properties:**

Colourfastness is the ability of dye to retain on fabric during washing, light exposure and perspiration etc. The washing, light were evaluated according to following the American Association of Textile Chemists and Colorists (AATCC) standards [13,14].

- Wash fastness using Launder O Meter (AATCC-110106)
- Light Fastness (AATCC test method 16-1993)
- Rubbing fastness was determined by Rubbing Fastness (IS: 766-1956) guidelines.

Colourfastness have determined by grades as 1-Very Poor, 2- Poor, 3- Moderately Good, 4- Good, 5- Excellent.

## Analysis of dye effluent

Effluents generated by natural dyes were collected after completion of above mentioned dyeing process. Natural dyeing effluent sample prepared by mixing the waste waters after dyeing and the adequate quantity was taken and transferring them in air tight bottle. Whereas effluents of synthetic dyeing were taken from chemical dyeing industry and local dyers hub in the air tight bottles.

pH and colour were observed at the time of collection. Effluents were analysed for Electrical conductivity (EC), Chemical Oxygen Demand (COD), Biological Oxygen Demand (BOD), Total dissolved solids (TDS), Total Suspended Solids (TSS), Total Hardness, Calcium (Ca), Magnesium (Mg) using American Public Health Association (APHA 22st Edition, 2012) guidelines and the results obtained were compared with central pollution control board, India standards [15]. Methods of dye effluent analysis are presented in Table 2.

Dhygical & Chamical Daysmotor	Mathad
Physical & Chemical Parameter	Methoa
Colour	Visual Comparison Method
Electrical Conductivity	Conductivity Cell Potentiometric Method
рН	Electrometric Method
Chemical Oxygen Demand	Open Reflux Method
Hardness	EDTA Titrimetric Method
Total Dissolve Solids	Gravimetric After Filtration
Total Suspended Solids	Gravimetric After Filtration Method
Biological Oxygen Demand	Wrinkler Method (3-Day Bod Test)
Calcium	EDTA Titrimetric Method
Magnesium	EDTA Titrimetric Method

Table 2. Dye effluent physicochemical parameters and methods
# Statistical analysis:

The data was analysed by using Microsoft office Excel 2007 (v12.0) .The data were expressed as mean  $\pm$ standard deviation, coefficient of variation (CV)[16].

# **RESULT AND DISCUSSION Dyeing of fabric**

Orange and dark green colourants were obtained from *Butea monsperma* and *Eucalyptus globulus* respectively. Banana pseudostem sap and *Punica granatum* rind extract were taken for the mordanting. For dyeing and mordanting of fabric, concentrations of mordants, pH, time and temperature of dyeing were selected through series of experimental trials. Constant dye concentration for dyeing was carried out for fabrics. However, the present investigation exhibited that both mordants have excellent efficiency to fix dye on fabric.

# **Evaluation of colour fastness:**

The evaluation of washing, light and rubbing of dyed cotton samples is presented in Figure 1. Good (4) washing fastness was obtained in *Eucalyptus* and *Butea* dyes with combination of *Musa sp*. Good to excellent (4-5) light fastness were showed by *Eucalyptus* + *Musa sp*. combination. The rubbing fastness results found moderately good to good (3-4) in *Eucalyptus* and *Butea* dyes with combination of *Musa sp*. All the test samples exhibited good to excellent (4-5) fastness except *Eucalyptus* + *Punica granatum* for rubbing and *Butea*+*Punica granatum* for washing.



\*Grades denoted as 1-Very Poor, 2- Poor, 3- Moderately Good, 4- Good, 5- Excellent.

Fig. 1 Colour fastness properties of dyed fabrics of natural dyes.

# Analysis of dye effluent:

Effluent samples were analysed for physico-chemical parameters is presented in the Table 3.

Parameter	Unit	Control	Effluents generated by Natural Dyes		Effluents generated by Synthetic Dyes		Permissible limit by CPCB
			Mean±SD	CV%	Mean±SD	CV%	
Colour	-	Clear	Dusty Orange	-	Blackish	-	-
Electrical Conductivity (EC)	µs/cm	245.8	299±9.8	3.2	431.3±20.0	4.6	-
pH	-	7.9	8.78±0.7	8.8	3.93±1.0	25.6	5.5-9.0
Chemical Oxygen Demand (COD)	mg/L	29.3	488.3±10.0	2.0	1876.3±14.2	0.7	250
Total Dissolve solid (TDS)	mg/L	562	1825±45	2.4	15530±88.8	0.5	-
Total Suspended solid (TSS)	mg/L	36.8	299±11.7	3.9	290 ±26.4	9.1	100
Biological Oxygen Demand (BOD)	mg/L	21.0	197.6±9.8	4.9	736±14.1	1.9	30
Calcium Hardness	mg/L	126	243.6±7.5	3.1	940.6±10.6	1.1	-
Magnesium Hardness	mg/L	164	193.6±4.5	2.3	1393±9.6	0.6	-
Total Hardness	mg/L	290	437.3±4.0	0.9	2333.6±20.26	0.8	-

Table.3 Physico-chemical analysis of natural and synthetic dyes effluents

\* CPCB-Central Pollution Control Board, India, SD- Standard Deviation, CV- Coefficient of variation

Effluent colour depends on dyes and mordants used in the dyeing process. The homogenous mixture of effluent gives darker shades of colour.

The electrical conductivity of water can be defined as the ability to conduct an electric current. EC is also an indirect measure of the saltiness of water [17]. Effluent EC of natural dyes and synthetic dyes found 299 ms/cm and 431.3 ms/cm respectively.

pH was recorded 8.78 in the effluent of natural dyes and 3.93 in the effluent of synthetic dyes. The pH of synthetic dye effluent is acidic in condition while alkaline in the case of natural dye.

Chemical oxygen demand is a measure of susceptibility to oxidation of the organic and inorganic matters present in water bodies and in the industrial and municipal effluents [18]. COD indicates the presence of all forms of organic matter, which can be biodegradable and non-biodegradable [19]. COD of effluent originated from natural dyes was observed 488.33 mg/L whereas synthetic dyes' effluent COD was observed 1876.33 mg/L. Both the types of effluents crossed the permissible limit by CPCB, India.

Inorganic salts and a small amount of organic matter present in water can be defined as total dissolved solids (TDS) [20].TDS of natural and synthetic dyes' effluent obtained as 1825 mg/L and 15530 mg/L respectively.

Suspended solids in water can be determined by filtration methods[21]. Both effluents are showing higher concentration than the permissible limit of CPCB, India.

Biological oxygen demand (BOD) of any water shows the presence of dissolved oxygen and its demand by the aquatic organism. As the value of BOD increased highly from 21.0 mg/L of control water and 30 mg/l of permissible limit as 197.6 mg/L in natural dyes and 736 mg/L in case of effluent discharged from the synthetic dyeing process.

The hardness of water is a measured content of dissolved calcium (Ca++) and magnesium (Mg++). They are only two divalent metal cations that occurred at an appreciable level in waters [22]. The total hardness of effluents was found 437.3 mg/L and 2333.6 mg/L in natural and synthetic dyes effluent respectively. Many epidemiological researchers have studied the relationship between risk for cardiovascular disease, growth retardation, reproductive

failure, and other health problems and hardness of drinking water or its content of magnesium and calcium [23].

BOD directly affects the amount of dissolved oxygen in rivers and streams. The greater the BOD, the more rapidly oxygen is depleted in the stream. This means less oxygen is available to higher forms of aquatic life. The consequences of the high BOD are the same as those for low dissolved oxygen aquatic organisms become stressed, suffocate, and die [24]. High levels of COD in water often correlate with threats to human health including toxic algae blooms bacteria from organic wastes and seafood contamination.[25] High COD levels decrease the amount of dissolved oxygen available for aquatic organisms. Low (generally under 3 mg/L) dissolved oxygen, or "hypoxia," causes reduced cell functioning, disrupts the circulatory fluid balance in aquatic species, and can result in the death of individual organisms as well as large "dead zones" [26,27]. High TSS can block light from reaching submerged vegetation. As the amount of light passing through the water is reduced, photosynthesis slows down. Reduced rates of photosynthesis cause less dissolved oxygen to be released into the water by plants. If the light is completely blocked from bottom-dwelling plants, the plants will stop producing oxygen and will die. As the plants are decomposed, bacteria will use up even more oxygen from the water. Low dissolved oxygen can lead to fish kills. High TSS can also cause an increase in surface water temperature because the suspended particles absorb heat from sunlight. This can cause dissolved oxygen levels to fall even further (because warmer waters can hold less DO) and can harm aquatic life in many other ways, as discussed in the temperature section [28].

Textile industries use lots of water in the whole dyeing process. Wastewaters discharged in drainage lines, canals, rivers, or soil. Water colour affects badly due to the high concentration of colouring matter in effluents. The physicochemical data in table 3 exhibiting that the pH, COD, TSS, and BOD of effluent generated by natural and synthetic dyes are exceeding the permissible limit stipulated by CPCB, India. The COD value recorded of natural and synthetic dyes effluent are approximately 2 and 7 times higher than the permissible limit respectively. The TSS value recorded of natural and synthetic dyes effluent are approximately 3 times higher than the permissible limit. The BOD value recorded of natural and synthetic dyes effluent are approximately 6.5 and 24.5 times higher than the permissible limit While hardness and total suspended solids are far more as compare to the control values. Data of both effluents also expressed that natural dyes effluents are very high in it. Yaseen and Scholz also studied that the synthetic dye effluents are high in colour, pH, suspended solids (SS), chemical oxygen demand (COD), biochemical oxygen demand (BOD) [29].

The addition of tannery and textile effluents in the soil system causes deflocculation of soil particles, increase in pH, sodicity, and increased EC reported by Chhonkar et al.[30]. Disposal of untreated waste water deteriorated soil quality as well as its fertility [31]

# CONCLUSION

The present work can be summarised as that the dyes and mordants obtained from natural sources are better options for successful colouring and good to excellent colour fastness properties. All water quality parameters of natural dyes effluent are better than that of synthetic ones. The use of natural resources as dyes and mordants would be safe for mankind and the environment due to their natural origin. Thus, the studies revealed the superior option of go green, sustainable ways of zero pollution to save water, soil and the whole nature in future.

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# FERTILIZERS AND PLANT PROTECTION USING BIOLOGICAL MEASURES

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#### ABSTRACT

In 2020, the EU proposed the new Green Deal strategy which is linked to the protection of the environment. At the same time, it sets new goals and commitments for the agricultural sector. One of the main tasks is reducing the input of mineral fertilizers and pesticides. The high use of pesticides and mineral fertilizers has prompted the search for rational, cost-effective and ecological strategies. Therefore, it is very important to evaluate the potential of organic fertilizers for crop yield and quality as well as to find alternatives to pesticides.

Fertilizers are one of the most important factors to achieve good productivity and quality of agricultural crops. Organic fertilizers are mainly derived from crop waste such as wheat straw or rapeseed residues and animal by-products such as animal waste, manure [1]. Different types of manure are usually used as organic fertilizers, but they may contribute to the environmental pollution. Pig, cattle or chicken manure can be used for biogas production [2]. Gas production process produces a substrate (digestate) that has more nutrients and is much more available to plants compared to raw manure [3]. One of the solutions to this problem could be the combined use of mineral and organic fertilizers. The use of digestate in combination with mineral fertilizers has been little studied.

One of the possibilities to reduce the use of pesticides could be allelopathic plants, which are not only potential sources of allelochemicals, but also renewable biomass sources. One of such plants is mugwort (*Artemisia dubia*). Mugwort possesses antimicrobial, insecticidal [4], phytochemical and antioxidant properties [5]. In Northern climate conditions, mugwort forms flowers but does not produce seeds. It is expected that the use of mugwort biomass and digestate may play a significant role in reducing the use of mineral fertilizers and pesticides.

Keywords: organic fertilizer, pesticides, mugwort.

## INTRODUCTION

In 2020, the European Commission announced a new Green agreement strategy on the environment. Set new targets and commitments for the agricultural sector. One of the main tasks is to reduce the amount of synthetic fertilizer and pesticides [6]. The high use of synthetic pesticides and fertilizers has led to the search for rational, cost-effective and environmentally strategies. Therefore, it is very important to evaluate the potential of organic fertilizers for crop yield and quality and to find alternatives to syntehetic pesticides.

The aim of this study was to analyse the impact of organic-mineral fertilizers on plants and soil and to review the alternatives of synthetic pesticides.

# METHODOLOGY

In this study, 34 scientific publications were analyse. The literature was collected from the WEB of Science Direct <u>https://www.sciencedirect.com/</u> and Springer LINK <u>https://link.springer.com/</u>. All reviewed literature sources were published from 2000 to 2021. The information in the database was searched using keywords: crops, soil, fertilize, organic fertilizer, mineral fertilizer, plants protection, pesticides and etc.

# RESULTS

## **Organic fertilizer**

Fertilizer is one of the most important measures to achieve the desired crop yield and quality. Increasing use of fertilizer contributes to the increase in food and feed production [7], but at the same time contributes to the deterioration of soil properties, increased water pollution and greenhouse gas emissions [8].

To reduce the negative impact of synthetic fertilizers on the environment, encourage to use of more organic fertilizers. The use of organic fertilizers is like accumulating crop yield and organic carbon [6,7,8]. Organic fertilizers together with microbes can improve the structure of soil, promote the accumulation of organic matter. Proper use of organic fertilizers can not only improve soil quality, but also promote plant growth and suppress soil borne diseases [12]. Organic fertilizer can be obtained from many composting and refining processes from waste such as manure, sewage sludge, biomass or food. [13,14].

One of the most common solutions for recycling organic waste is a biological process that converts organic matter into biogas and residues called digestate (Fig. 1) [15] [16].



Figure 22. Anaerobic digestion process and products [17]

A digestate can be described as a mixture of water and solids dissolved in organic and inorganic materials [18,19]. Manure, plant residues, waste, food industry and special energy crops are the main raw materials for anaerobic digestation in biogas companies. Anaerobic digestion is a reliable organic waste management technology and one of the most promising renewable energy production processes. Waste from the processing process, such as digestate, can be used as agricultural biological fertilizers [20]. Because it is rich in mineral elements (nirogen, phosphorus, potassium) and is part of the organic matter, which has a positives effect on the chemical and physical properties of the soil [19] and increases productivity [21]. The rate of action of the digestate as a fertilizer can be compared to that of a mineral fertilizer [18,19]. It can increase the amount of organic carbon in the soil [22]. Chiew and others scientists have found that the use of digestion as a fertilizer increases the amount of macro- and micronutrients in the soil and plants.

## **Organic – mineral fertilizer**

Optimizing mineral and organic fertilizers to increase crop yield and soil organic carbon is a priority. However, it is still unclear how to achieve this goal, as crop yield and the response of organic carbon to the use of synthetic and organic fertilizers vary depending on climate, soil type, fertilization history and the amount of carbon and nutrients already present in the soil. [10]. Organic fertilizers often contain low levels of nutrients, which means they meet the nutrients requirements of the crop less and cause temporary embolization after use. However, the impact of organic fertilizers on crop yields is slow and variable over time [9]. Therefore, mineral fertilizers can supplement the nutrient supply of organic matter. [23]. Zhao and other scientists are among the first to conducting research on pig manure and synthetic fertilizers. Their study proved the composition of organic and mineral fertilizers and succeeded in increasing crop productivity, soil nutrient availability [24], microbial biomass, enzymatic activity, nitrogen processes, community richness and diversity [25]. Zhang and other researchers confirmed that the right combination of synthetic fertilizers and cow manure can increase crop yields as well as maintain good soil properties [11].

## **Plant protection**

Plant protection plays a key role in increasing crop productivity to achieve this goal [6]. Crop protection measures are to preserve and ensure a certain yield and quality standards that are generally available to prevent pests, diseases and weeds [26]. The time nowadays is to reduce the negative synthetic pesticides and its impact on people and the environment.

Ecological crop protection includes biological methods based on specific microorganisms or natural compounds derived from plants [27]. An analysis of the article by Lengai and other researchers suggested that the use of botanical pesticides is recommended to minimize the effects of synthetic pesticides. Which are derived from plants belonging to different families are used as plant extracts or essential oils. Botanical pesticides can be used to produce plant bark, leaves, roots, fruits, seeds, flowers and etc. Parts of the plant are selected from the active compounds and their abundance in a particular part [28].

# An alternative of synthetic pesticides

One way to reduce the use of synthetic pesticides could be the use of allelopathic plants, which are not only potential sources of allelochemicals but also renewable biomass. Artemisia genus belongs to the family Asteraceae and includes more than 500 species, they are prevalent in various regions of the world [29]. Plants of this genus are mostly used in medicine, but are increasingly delving into their essential oils, which can have a pesticidal effect [30]. One of these is the perennial, known as strong-smelling plant - mugwort (Artemisia dubia)[31]. With these plants are very little research carried out, usually found in the literature is Artemisia vulgaris, Artemisia annu, Artemisia absinthiums and etc. [5,31–33]. Mugwort like other plants of the genus Artemisia has antimicrobial, insecticidal [4], phytochemical and antioxidant properties [5, 28, 33,34]. In northern climates, shade hardness forms flowers but does not mature seeds. Mugwort, like other plants in the Asteraceae family, is an extremely rich source of biologically active compounds such as polyphenols, terpenes, and flavonoids. These bioactive compounds, which are very important plant secondary metabolites, have specific properties. Phenols and flavanoids, also called secondary metabolites, are the main allelochemicals found in plants with allelopathic activity. In the literature on this topic, low concentrations of phenolic compounds are called plant germination and growth stimulants because they can act as antioxidants. [30]. According to Polish scientists, plants of the Asteraceae family can be as biostimulants, which can not only stimulate seed germination, but also protect against adverse conditions or stress. [31]. Allelopathic plants such as artemisia dubia can be widely used in sustainable and organic agriculture due to their potential role not only in controlling weeds and pests, but also in promoting crop growth and development [31].

# CONCLUSIONS

It is very important to reduce the use of synthetic fertilizers and pesticides or even finding an alternative. This review has shown that is possible to know the use of synthetic fertilizers in combination with organic fertilizers. Anaeorobic digestion of manure or waste results in a digestate that is rich in mineral elements and its activity can be equated to a synthetic fertilizer. Proper combination of synthetic fertilizers and digestate can increase yields and at the same time reduce the use of synthetic fertilizers.

This review also provides an alternative to the use of synthetic pesticides. Plants of the *Asteraceae* family that have the potential to evaluate of mugwort biomass as a natural pesticide, but such studies have not been performed. It is therefore important to evaluate the potential uses of this plant.

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# EFFECTS OF MICROPLASTICS ON FISH: A REVIEW ON GENOTOXICITY OF AN ANTHROPOGENIC POLLUTANT

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#### ABSTRACT

The presence of plastic pollution, especially microplastic (MP), in the marine environment is a growing problem that researchers are facing today. In 2018 it has been estimated that the global plastic production has reached 359 million tons. Unfortunately, effects of MP on living organisms are greatly understudied in animal models. Various studies have shown that a large range of marine animals, including fish, are susceptible to MP ingestion. However, only a few studies investigated the potential genotoxic and cytotoxic effects of MP and the consequences of long-term exposure, especially on the development in early life stages. Not only MP itself but various toxic additives are also a source of concern. In this paper, a comprehensive review of the literature has been conducted with the following objectives: (1) to summarise the properties, and sources of MP; (2) to describe methods by which genotoxic and cytotoxic effects were assessed; (3) to summarise the results of individual experiments where fish models were used; (4) to explain a potential mechanism how MP can cause genetic damage by inducing oxidative stress; (5) to discuss how MP can change the bioavailability of other toxic pollutants, pathogens, and act as a vector in their transfer. Effects of MP range from inflammation to behavioural and developmental problems in fish so research in this field is essential.

Keywords: microplastic, pollution, ecotoxicology, marine environment, genotoxicity

# **INTRODUCTION**

The occurrence of plastic particles in the aquatic ecosystems have been documented since 1970s [1] and some researchers as early as 1972 already reported the ingestion of 0.5 millimetre polystyrene spherules by fish [2]. Since then, global plastic production reached 359 million tons in 2018 and increased to 368 million tons in 2019 [3]. Frias and Nash (2019) suggested to define microplastic (MP) as "any synthetic solid particle or polymeric matrix, with regular or irregular shape and with size ranging from 1  $\mu$ m to 5 mm, of either primary or secondary manufacturing origin, which are insoluble in water" [4]. Meanwhile the Joint Group of Experts on the Scientific Aspects of Marine Environmental Protection (GESAMP), officially defines MPs simply as "plastic particles <5 mm in diameter" [5]. In the last couple of decades, the presence of MP in aquatic ecosystems became a recognized and growing problem. Since 2009 publications with keyword "microplastic" grew exponentially (Fig. 1).



Source, web of Science (a tool from Clarivate Analytics, 2021)

Fig. 1. Web of Science (a tool from Clarivate Analytics, 2021) search (February 2, 2021) using the keyword "microplastic". Results are shown from 1990 to 2020. The search resulted in 3093 publications in total.

Recent studies reveal that MP is abundant and widespread in freshwater, estuarine and marine environments worldwide: from polar regions [6] to the deep sea [7].

A large number of studies demonstrated MP ingestion by variety of aquatic animals including zooplankton [8], crustaceans [9], molluscs [10], annelids [11], fish [12], turtles [13], seabirds [14] and marine mammals [15]. Despite their presence in fish, understanding of the adverse effects of MPs remains lacking. Especially non-ingestion related exposure and cytogenetic effects.

The main objectives of this review are to summarise the literature about properties, and sources of MP, describe nuclear abnormalities and the comet assay methods, investigate the results of individual experiments as well as discuss potential mechanisms of MP genotoxicity and associated damage.

# SOURCES AND PROPERTIES OF MICROPLASTIC

#### Sources of microplastic

MPs can be found in everyday domestic products such as exfoliating facial scrubs, toothpastes [16], synthetic clothes (textile fibres) [17] or produced for industrial applications such as resin pellets used in the plastic industry (primary microplastics) [5]. Another source of MP is fragmentation of larger plastic pieces (secondary microplastics) [16].

Land-based sources, storm sewers and runoffs account for about 80-85% of MP contamination in marine ecosystems [16] [18]. About 18% of MP in marine environments is brought by the fishing industry [18] in the shape of ALDFG (Abandoned, Lost or otherwise Discarded Fishing Gear).

#### **Properties of microplastic**

MP includes a wide range of synthetic polymers that are usually described by their morphological characteristics: size, shape (e.g., microbead, fibre, film, and irregular), density, colour [17] [19] [20]. It is believed that these characteristics as well as composition of MP can alter toxic responses [21]. Size is a key characteristic that contributes to the bioavailability of MP [19]. For fish, the bioavailability process includes two routes of uptake: direct - ingestion or indirect - trophic transfer. Lu and colleagues (2016) demonstrated that uptake and tissue

accumulation of polystyrene microplastics (PS-MPs) in *Danio rerio* after 7 days of exposure depended on the size of the particles. 5  $\mu$ m PS-MPs were found in fish gills, liver, and gut while 20  $\mu$ m PS-MPs were only detected in fish gills and gut with no trace in liver [22]. Density of particles controls what fish will be affected by what type of MP. Fish living in the upper water column are more prone to encounter low-density plastics like polyethylene (PE), while benthic fish are more susceptible to high-density plastics like polyvinyl chloride (PVC) [19]. Peters and colleagues (2017) results show how six marine fish species ingested MP based on shape: fibre (86.4%), microbead (12.9%), and fragment (< 1.0%) [23]. Another study by Boerger *et al.* (2010) demonstrated that the most abundant ingested MPs were white, clear, and blue mainly because those are the colours of plankton which is the main food source for pelagic fish [24]. Nelms *et al.* concluded that tropically transmitted MP has implications for human health [25].

## Nanoplastic

Nanoplastics (NPs) introduce more severe risk since their size allows them to enter cells by endocytosis [18] [26]. The definition of NP is still debatable and various researchers have set the upper size limit at either 1000 nm or 100 nm [27]. Although research on MP is increasing dramatically literature on effects of NPs especially considering marine animals is still limited [28]. Toxicity of NP is usually researched in *D. rerio* and it is proposed to be a great model organism in this field [29].

# **REVIEW OF METHODOLOGY**

There is plenty of biomarkers in animal models to assess *in vivo* and *in vitro* toxicity of various substances (fish mortality/recovery rates, hepatic parameters, acetylcholinesterase assay for testing neurotoxicity, lipid peroxidation and *etc.*). Since this review focuses on genotoxicology, the main two cytogenetic methods will be described: micronucleus (MN) and other nuclear abnormalities test and single-cell gel electrophoresis assay (SCGE or the "comet" assay). Despite the method, it is crucial to mention that in ecotoxicological studies concentration is an essential parameter. The use of unrealistic exposure concentrations represents an aggravating factor in the toxicological assay, highlighting the importance of *in natura* approaches for the environmental toxicity assessment [26] [30].

# Micronucleus and other nuclear abnormalities test

The first MN test applied to fish model was done by Hooftman and Raat (1982) who carried out research with the eastern mudminnow (*Umbra pygmaea*) [31]. Before used methods (the chromosome aberration and the sister-chromatid exchange tests) were effective and accurate but time-consuming and difficult with many fish species which have rather large numbers of small chromosomes [32]. Since then, sufficient amount of new protocols and modifications to the MN test have been proposed [33]. In general, MN test is used to detect compounds in aquatic ecosystems that could have clastogenic or aneugenic effects and cause chromosomal DNA damage [34]. Micronuclei are induced by errors in cell division when fragments of chromosomes or entire chromosomes lag and are not incorporated into daughter cell nuclei mainly because of defects in centromere, lack of centromere, chromosomal aberrations or errors in cytokinesis [35] [36]. MN test is carried out by scoring cells that have one or more MN [35]. Majority of studies in fish have used peripheral erythrocytes, but other tissues are also used (e.g., liver, gill, kidney) [35]. Besides MN, studies have used other nuclear abnormalities (NAs) as well (e.g., lobed, notched, blebbed (BL) and eight-shaped nuclei, nuclear buds (NB), nuclear buds on filament (NBf), bi-nucleated cells (BN), bi-nucleated cells with nucleoplasmic bridges, fragmented apoptotic (FA) cells and etc.) [37] [30] [38]. Nuclear abnormalities, such as NB, NBf and BL, are associated with MN [39] [40] and are markers of chromosomal instability events, e.g. NB as a biomarker of elimination of amplified DNA and/or DNA repair complexes. Other, NAs have been associated with various degenerative nuclear changes and failure in normal cell division.

## The comet assay

In the field of environmental toxicology fish were one of the first animal models to which the comet assay was adopted [41]. Since then, the comet assay became one of the most frequently used tests for detecting and quantifying DNA strand breaks [42]. Just like MN test, the comet assay can be applied to various cell types: erythrocytes and cells of gill, liver, kidney, gut. It is worth mentioning that in fish studies erythrocytes are most commonly used [43]. The comet assay is carried out by suspending cells in a thin agarose gel, lysing the cells using detergents and staining with fluorescent DNA binding dye. After that, electrophoresis is run, and broken DNA segments migrate further than the nucleus [43]. Modifications using alkaline conditions allow detection not only of single strand breaks but also of double strand breaks [41]. Usually, there is a positive correlation between the results of the comet assay and MN test because the comet assay determines primary DNA damage while MN test reflects non-repaired or inappropriately repaired primary DNA damage [44]. The comet assay has many advantages and has been used in both laboratory and field-based studies [42].

# EXPERIMENTAL EVIDENCE OF MP AND NP GENOTOXICITY

Probably one of the most significant studies done in the field of MP genotoxicity on fish was published by Jakubowska *et al.* (2020). They assessed effects of chronic (113 days) exposure to three most mass-produced polymers: polystyrene (PS), polyethylene terephthalate (PET) and polyethylene (PE). In this study sea trout (*Salmo trutta*), from fertilized eggs to mobile yolk-sac larvae, was used as an experimental animal. This study is important for five main reasons: i) environmentally realistic concentrations of MP were used, ii) effects on early life stages were researched, iii) non-dietary exposure was studied because seat trout larvae feed endogenously, iv) the exposure was long-term, v) ecologically and economically important fish species were used (majority of research beforehand was done on model species like *D. rerio*). Experimental setup consisted of freshwater control and three treatment groups (PS, PET and PE). Total genotoxicity levels (assessed as the sum frequencies of MN, NB, and BL) were significantly higher in all treatments compared to the control. In all treatment groups significant formation of NB was observed while significantly higher frequencies of MN and BL were observed in PS and PET groups. No significant differences in 8-shaped nuclei formation were detected while FA and BN erythrocytes were not observed at all [30].

Pannetier and colleagues (2019) used Japanese medaka (*Oryziaz latipes*) embryos and prolarvae to assess the toxicity of environmental samples of MPs. DNA damage was assessed using the comet assay and for the embryo exposure no significant variation in DNA strand breaks was found after 8 days of exposure. Meanwhile 48 h MP-exposed prolarvae showed significant increase in DNA strand breaks and MPs from different sampling locations induced different patterns of toxicity. The absence of toxic effects of the virgin MP extract in this experiment was explained by an observation that environmental MP samples most likely caused adverse effects due to the contaminants and sorbed pollutants [45]. One year later another study by the same authors was published in which they used a similar experimental design but this time they carried out experiments by feeding Japanese medaka larvae and juveniles with environmental MP samples and studying ingestion related exposure. A significant induction of DNA strand breaks was observed in larvae fed MP-contaminated food compared to the control

group. Juveniles also showed a significant increase of DNA strand breaks in fish exposed to food contaminated with environmental samples of MPs [46].

A study using rainbow trout (*Oncorhynchus mykiss*) cell lines by Bussolaro *et al.* (2019) explored toxicity of PS MP co-exposure with polycyclic aromatic hydrocarbon (PAH) contaminants. No significant fluctuations in DNA damage in gill cell line (RTgill-W1) were observed. However, in gut cell line (RTgutGC) the presence of MPs significantly increased 3-nitrobenzanthrone-induced DNA damage but had no effect on benzo[a]pyrene-treated cells. Enhancement of PAHs induced DNA damage in the presence of MPs indicates uptake of MPs by the cells. Interestingly, MPs alone did not increase DNA damage, but it can be hypothesized that PAH bound to MPs may alter their capability to induce genotoxic effects as well as MPs can alter genotoxicity of PAHs. It is important to notice that concentrations of MPs and PAHs used in this study exceeded those detected in the environment [47].

Roda *et al.* (2020) investigated potential interactions of PE MP and copper (Cu) on streaked prochilod (*Prochilodus lineatus*). The alkaline comet assay was performed with erythrocytes, gill, and hepatic cells. Frequencies of MN and other NAs in erythrocytes were also assessed. Fish showed significantly higher DNA damage after 96 h of exposure to MP, Cu and MP + Cu groups compared to the control. Authors suggest that the variation of results in different cell types could be due to diversity of repair mechanisms as well as metabolic activity and antioxidant defence ability. No significant alterations in MN and NAs frequencies were observed in all treatment groups [48].

Regarding NP Estrela and colleagues (2021) examined toxic effects of PS NP alone and in combination with ZnO nanoparticles (ZnO NPs) on grass carp (*Ctenopharyngodon Idella*). All treatment groups (ZnO NP and PS NP alone or in combination) showed significant increase in DNA damage assessed by the comet assay. Authors noticed no synergistic, antagonistic, or additive action of pollutants combination after 3 days of exposure and pollutants had similar genotoxic effects [49].

The toxicity of PS NP alone was assessed on grass carp juveniles by Guimarães *et al.* (2021). Fish were exposed at environmentally relevant concentrations for 20 days. Both the comet assay and MN test were carried out. The results showed a significant dose-depended induction of DNA damage in treatment groups. This demonstrates that increased NP concentrations lead to increased damage to DNA integrity. The increased frequencies of MN and other NAs (BN cells, nuclear constrictions, BL, notched kidney-shaped and displaced nuclei, as well as nuclear vacuole, among others) were observed in all juveniles exposed to PS NP [50].

Finally, Brandts and colleagues (2021) investigated short-term (96 h) exposure to polymethylmethacrylate (PMMA) NP on the gilthead seabream (*Sparus aurata*). This study used documented environmental concentrations of MPs because information about environmental concentrations of NPs is not available. The total NAs frequency was significantly higher after 24 h and after 96 h of exposure compared to the control. The authors noted that damage observed at 24 h of exposure could be related to direct NP action on cells while increased NA induction at 96 h might be related to formation of reactive oxygen species [51].

# **RISK OF MICROPLASTIC**

## **Oxidative stress**

It is now well documented that MP itself can induce oxidative stress, generate reactive oxygen species (ROS) and many researchers believe that MP ability to generate ROS is the main mechanism by which MP causes genetic damage [20] [30] [50] [51]. In majority of the studies where genetic damage was assessed, oxidative status was evaluated as well and positive

correlation was observed [48] [49] [50] [51]. Exposure to ROS for extended periods of time causes oxidative damage even in the presence of antioxidant enzymes [20] so exposure time is an essential parameter when discussing MP toxicity. Another consequence of ROS is lipid peroxidation which causes damage to cellular membrane, changes membrane permeability [52] and this way further increases the entrance of different pollutants into the cells [20]. NPs experimentally induced even stronger oxidative stress compared to MPs [52].

# **Microplastic additives**

Not only polymers by themselves but various toxic additives are another source of concern. For example, even though MPs are biochemically inert [17], depending on their properties (size, density) fragmentation can still happen primarily by UV-B radiation which starts photo-oxidative degradation [18]. For this reason, during plastic production ultraviolet stabilizers and antioxidants are used as additives to enhance chemical properties and lifespan of polymers [53]. As MP goes through many manufacturing processes, it is essential to assess the toxicity of these additives [17] [26]. Manufactured MPs can slowly leach out various additives that eventually end up in aquatic ecosystems and affect living organisms [18]. One of the best documented examples of toxic additives is benzo[a]pyrene [47].

# Microplastic as a vector

Aquatic ecosystems already contain numerous persistent organic pollutants (POPs), pesticides, toxic metals, and other hydrophobic pollutants [16] [17] [18]. POPs are known to be genotoxic, mutagenic and carcinogenic [20] but usually are found at very low concentrations in natural environments [18]. Unfortunately, because of large surface area of MPs they have higher capacity to sorb various pollutants to the surface this way increasing their concentration [16] [17] [18]. These contaminated MPs provide an easy route for POPs and other pollutants to enter not only exposed organism but food web as well and this way leading to biomagnification of these substances at higher trophic levels [16] [18]. In addition, MPs can serve as a vector for bacterial biofilms and other pathogens [17].

# CONCLUSIONS

This review summarized relevant aspects and studies involving MP and fish models. This should expand our understanding that impacts of MPs, their additives and sorbed pollutants go beyond direct damage to the fish's gut and digestive system. For better awareness of the adverse effects of MPs and NPs in aquatic environments further research is required.

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# SYNTHESIS OF ORDERED MESOPOROUS SILICAS IN DYE ENRICHED AQUEOUS SOLUTIONS

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#### ABSTRACT

Template-assisted sol-gel synthesis of aminosilicas of MCM-41 type was carried out in the presence of micelles of long-chain quaternary ammonium salt as structure-directing agent in the azo dye enriched aqueous medium. Structural parameters of synthesized materials were estimated by low-temperature nitrogen adsorption-desorption and x-ray diffraction analysis. It was found that the incorporation of azo dyes in micelles of long-chain alkyltrimethyl ammonium salt causes an increase of surface area and contraction of pore diameter of resulting aminosilicas. In general, azo dyes positively impact the formation of hexagonally ordered mesoporous structure of MCM-41-type silicas due to the simultaneous interaction with the micellar and extra-micellar environment. Obtained results demonstrate the possibility of dye-enriched aqueous solutions reuse for sol-gel synthesis of silica materials with improved structural characteristics.

Keywords: azo dyes; micellar solubilization; MCM-41; sol-gel synthesis; mesoporous structure

# **INTRODUCTION**

Intensive usage of toxic artificial colorants in dyeing industry causes huge environmental pollution problems. Therefore, it is essential to improve approaches aimed at the purification or reuse of wastewater. In our opinion, environmentally benign and economically beneficial to reuse enriched waste solutions produced after dyeing procedures for the synthesis of silicas with ordered mesoporous structure.

It is known that silica materials with hexagonally arranged mesoscale pore structure are usually prepared in aqueous solutions of surfactants, which form micellar aggregates directing sol-gel condensation of silicate species [1–7]. Long-chain quaternary ammonium salts belong to the most widely used structure-directing agents at sol-gel synthesis of hexagonally arranged mesoporous silicas of MCM-41 type. Regulation of surfactant aggregates composition and, consequently, pore dimensions of silica materials obtained by sol-gel condensation of structure-forming silanes can be realized by adding of auxiliary organic compounds into the reaction medium. Effects caused by incorporation of alkylamines with short and long alkyl chains [8, 9], short-chain alcohols [10, 11], primary alcohols with medium chain lengths [12], bulky aromatic species [13, 14], hydrocarbons [15, 16] into the hydrophobic interiors of long-chain alkylammonium salts aggregates on the formation of hexagonally arranged mesoporous silica structure were studied over the past decades.

Micellar solubilization of dye molecules from aqueous solutions affects critical micelle concentration and configuration of surfactant micelles [17–19]. Therefore, using of dye enriched solutions may alter micellar aggregates and induce substantial changes in the mesoporous structure of silica materials prepared by template-assisted sol-gel synthesis. However, up to now, the introduction of dye additives in templated sol-gel synthesis of silica materials was carried out in order to combine their optical properties with the convenience of solid silica matrix possessing arranged mesoporous structure [20-22]. Therefore, in the present work, we focused our attention on the impact of azo dye additives used in template-assisted sol-gel synthesis on the structural parameters of MCM-41-type aminosilicas. Obtained results

demonstrate principle possibility of MCM-41 mesoporous structure regulation by introduction of dye additives into sol-gel synthesis and can be useful in design of functional silica materials with improved structural characteristics.

# METHODOLOGY

# Materials

Tetraethyl orthosilicate (TEOS) (from Merck, purity  $\ge 99\%$ ) and (3-aminopropyl)triethoxysilane (APTES) (from Merck, purity  $\ge 99\%$ ) were used as the silica source, whereas, cetyltrimethylammonium bromide (CTAB) (from Merck, purity  $\ge 97\%$ ) was used as structure-directing agents in sol-gel synthesis. Methyl red (MR) (from Reakhim, analytical grade) and alizarin yellow (AY) (from Acros,  $\ge 96\%$ ) were used as auxiliary agents in template-assisted sol-gel condensation of silanes. Aqueous ammonia 25% (from Reakhim, analytical grade) and ethanol 96% (from Reakhim, chemical grade) were used as solvents without additional purification. Hydrochloric acid 37% (from Reakhim, chemical grade) was used along with ethanol 96% for template extraction as received.

# Sol-gel synthesis of MCM-41-type aminosilicas

Templated sol-gel synthesis of MCM-41-type mesoporous aminosilicas was realized in the presence of micelles of long-chain quaternary ammonium salt, CTAB, as structure-directing agents in water-ethanol-ammonia medium (Table 1).

Silica	Molar composition of the reaction mixture	Content of 3-aminopropyl groups (mmol·g <sup>-1</sup> )
NH <sub>2</sub> -SiO <sub>2</sub>	0.096 TEOS : 0.004 APTES : 0.012 CTAB : 0.54 NH <sub>4</sub> OH : 14.4 H <sub>2</sub> O	0.28
NH <sub>2</sub> -SiO <sub>2</sub> /AY-4%	0.096 TEOS : 0.004 APTES : 0.004 AY : 0.012 CTAB : 0.54 NH <sub>4</sub> OH : 14.4 H <sub>2</sub> O	0.22
NH <sub>2</sub> -SiO <sub>2</sub> /AY-10%	0.09 TEOS : 0.01 APTES : 0.004 AY : 0.012 CTAB : 0.54 NH <sub>4</sub> OH : 14.4 H <sub>2</sub> O	0.70
NH2-SiO2/AY-50%	0.05 TEOS : 0.05 APTES : 0.004 AY : 0.012 CTAB : 0.54 NH <sub>4</sub> OH : 14.4 H <sub>2</sub> O	1.17
NH2-SiO2/MR-4%	0.096 TEOS : 0.004 APTES : 0.004 MR : 0.012 CTAB : 0.54 NH <sub>4</sub> OH : 14.4 H <sub>2</sub> O	0.29

Table 1. The molar composition of reaction mixture and content of surface functional groups of MCM-41-type aminosilicas

To prepare parent NH<sub>2</sub>-SiO<sub>2</sub> silica, the batch of CTAB was placed into a conical vessel and dissolved in mixture of deionized water and ethanol. After that, a 25% aqueous solution of ammonium hydroxide was poured into the reaction vessel and mixture of TEOS with APTES was slowly added in sol-gel medium for 15 min under vigorous stirring. The resultant reaction slurry was stirred at 273 K for two hours, then transferred to a polypropylene bottle and aged at 373 K without stirring for 24 h.

Sol-gel synthesis of  $NH_2$ -SiO<sub>2</sub>/AY and  $NH_2$ -SiO<sub>2</sub>/MR silicas with incorporated dye moieties was carried out by base-catalyzed sol-gel condensation of silanes mixture, TEOS and APTES, in the presence of micellar system containing CTAB and AY or MR (Table 1).

After hydrothermal treatment, synthesized silicas were filtered, washed with deionized water, and dried in air at 373 K for two hours. Removal of long-chain quaternary ammonium

salt and molecules of dyes physically sorbed on the pore walls of mesoporous silicas was performed by extraction in acid-ethanol medium.

# Characterization of MCM-41-type aminosilicas

The porous structure of synthesized MCM-41-type aminosilicas was characterized using data of low-temperature adsorption-desorption of nitrogen at T = 77 K with a Kelvin-1042 Sorptometer. Aminosilicas were outgassed under vacuum at 413 K for 20 h and then analyzed in the region of relative pressures from 0.06 to 0.99 in increment of 0.015. The specific surface area *S*<sub>BET</sub> was evaluated according to the multi-point Brunauer-Emmett-Teller (BET) method [23]. The non-local density functional theory (NLDFT) was applied to obtain the pore size distribution from the adsorption branch of isotherm assuming cylindrical pore structure of silica materials and evaluate the pores diameter *D* [24]. The total pores volume *V* was determined from the amount of adsorbed nitrogen at a relative pressure equal to 0.99 [25].

X-ray diffraction spectra were registered using a diffractometer DRON-4-02 with monochromatic CuK<sub> $\alpha$ </sub> emission ( $\lambda = 0.15418$  nm) and nickel filter.

The content of surface 3-aminopropyl groups was estimated from the results of the potentiometric titration with 0.01 M HCl [26]. For this, the batch of mesoporous organosilica was placed into a volumetric flask and poured with 0.01 M HCl. The obtained suspension was stirred at 294 K for 24 h to attain equilibrium. pH of starting and equilibrium solutions were measured by an Ionometer I-120.1. The content of 3-aminopropyl groups chemically immobilized on silica surface was calculated by Equation [27]:

$$C_{NH_2} = \frac{(10^{-pH_1} - 10^{-pH_2}) \cdot V}{m},$$
(1)

where  $C_{NH_2}$  – the content of 3-aminopropyl groups of mesoporous silica, mol·g<sup>-1</sup>;  $pH_1$  and  $pH_2$  – the pH of starting and equilibrium solutions, respectively; V – the volume of solution, 1; m – the batch of mesoporous silica, g.

# **RESULTS AND DISCUSSIONS**

The isotherms of nitrogen adsorption-desorption as well as the pore size distributions of  $NH_2$ -SiO<sub>2</sub>,  $NH_2$ -SiO<sub>2</sub>/AY, and  $NH_2$ -SiO<sub>2</sub>/MR silicas are shown in Figure 1. It can be seen that the profiles of isotherms differ noticeably in dependence of molar composition of reaction mixture used in the process of sol-gel synthesis (Fig. 1, Table 1). The isotherm of nitrogen adsorption-desorption on  $NH_2$ -SiO<sub>2</sub> belongs to the type II with hysteresis loop of the type H3 according to the IUPAC classification (Fig. 1a). A linear increase in nitrogen adsorption, which is observed at relative pressures up to 0.25, can be attributed to the monolayer formation on mesoporous walls. The pore size distribution curve calculated by the NLDFT model reveals that single mesopore diameter is prevailing in  $NH_2$ -SiO<sub>2</sub> silica (Figure 1a, Table 2).



Fig. 1. Low-temperature nitrogen adsorption-desorption isotherms and pore size distributions (inserts) for NH<sub>2</sub>-SiO<sub>2</sub> (a), NH<sub>2</sub>-SiO<sub>2</sub>/AY-4% (b), NH<sub>2</sub>-SiO<sub>2</sub>/MR-4% (c)

Introduction of azo dye additives as co-surfactants in sol-gel synthesis of aminosilicas causes noticeble changes in the profiles of low-temperature nitrogen adsorption-desorption isotherms as well as the pore size distributions of NH<sub>2</sub>-SiO<sub>2</sub>/AY-4% and NH<sub>2</sub>-SiO<sub>2</sub>/MR-4% silicas in comparison with parent NH<sub>2</sub>-SiO<sub>2</sub> (Figure 1). It can be seen that the isotherms belong to the type IV with hysteresis loop of a type H3 according to the IUPAC classification (Figure 1b,c). A linear increase in nitrogen adsorption, followed by the sharp rise of isotherm curves at relative pressures from 0.25 to 0.35, is typical for MCM-41 silicas with hexagonally arranged mesoporous structure. The pore size distributions of silica materials reveal that uniform mesopores with single mesopore diameter are formed (Figure 1, Table 2). Introduction of moderate amounts of organic additives in sol-gel reaction medium leads to the improvement of the mesoporous structure of resulting NH<sub>2</sub>-SiO<sub>2</sub>/AY-4% and NH<sub>2</sub>-SiO<sub>2</sub>/MR-4% silica materials. Along with distinct inflection step on the nitrogen adsorption isotherms, noticeable narrowing of pore size distribution is observed (Figure 1).

Silica	$S_{BET} (m^2 \cdot g^{-1})$	$V(\mathrm{cm}^3\cdot\mathrm{g}^{-1})$	D (nm)
NH <sub>2</sub> -SiO <sub>2</sub>	515	0.91	3.78
NH <sub>2</sub> -SiO <sub>2</sub> /AY-4%	622	1.06	3.78
NH <sub>2</sub> -SiO <sub>2</sub> /AY-10%	339	0.75	3.54
NH <sub>2</sub> -SiO <sub>2</sub> /AY-50%	406	0.72	3.78; 4.89; 6.08
NH <sub>2</sub> -SiO <sub>2</sub> /MR-4%	608	0.80	3.78

Table 2. Parameters of MCM-41-type aminosilicas structure calculated from low-temperature adsorption-desorption of nitrogen

The x-ray diffraction pattern of  $NH_2$ -SiO<sub>2</sub> silica has only one low-intensity reflection from the (100) plane at 2 $\theta$  equal to 2.25 deg (Figure 2). This indicates the formation of a disrupted hexagonal arrangement of pore channels in NH<sub>2</sub>-SiO<sub>2</sub>. Contrariwise, the addition of azo dyes co-templates at sol-gel synthesis of aminosilicas causes substantial improvement of mesoporous structure. According to the results of x-ray diffraction studies (Figure 2), strong diffraction peak from the (100) plane at 2 $\theta$  equal to 2.1 deg as well as two low-intensity (110) and (200) reflections are registered on the diffractograms of NH<sub>2</sub>-SiO<sub>2</sub>/AY and NH<sub>2</sub>-SiO<sub>2</sub>/MR silicas. Similar positive effect of phenolphthalein additive on the ordering of silica mesoporous structure was registered in the work [22] due to the strong interactions of structure-directing agent CTAB and indicator dye species.



Fig. 2. X-ray diffraction patterns of NH<sub>2</sub>-SiO<sub>2</sub> (curve 1), NH<sub>2</sub>-SiO<sub>2</sub>/AY-4% (curve 2), NH<sub>2</sub>-SiO<sub>2</sub>/MR-4% (curve 3)

It is known that the molar composition of the reaction sol-gel mixture has a noticeable impact on the structural characteristics of the resulting silica material. The presence of azo dye additives may change mesopore channels size and ordering due to the influence on the stability of supramolecular aggregates formed by the incorporation of dye into the CTAB micelles. Therefore, estimation of the critical quantity of dye additive that can be used as co-template at sol-gel synthesis of aminosilica materials without loss of mesoporous structure ordering is of significant interest. As can be seen from Figure 3, the pore size distributions of silica materials reveal that introduction of increasing amounts of AY results in a noticeable transformation of mesoporous structure.



Fig. 3. Low-temperature nitrogen adsorption-desorption isotherms and pore size distributions (inserts) for NH<sub>2</sub>-SiO<sub>2</sub>/AY-10% (a) and NH<sub>2</sub>-SiO<sub>2</sub>/AY-50% (b)

The content of pores with a diameter greater than 5 nm increases in the series NH<sub>2</sub>-SiO<sub>2</sub>/AY- $4\% < NH_2$ -SiO<sub>2</sub>/AY- $10\% < NH_2$ -SiO<sub>2</sub>/AY-50%. In other words, pore size distribution confirms that the pores with diameter of 3.78 nm are prevailing in NH<sub>2</sub>-SiO<sub>2</sub>/AY-4%, whereas structure of NH<sub>2</sub>-SiO<sub>2</sub>/AY-50% silica is formed by a wide range of mesopores (Fig. 1, 3, Table 2). Analysis of low-temperature nitrogen adsorption-desorption isotherms and pore size distributions clearly indicates that an increase in AY content from 4 to 50 mol% leads to the undesirable decrease of surface area, pore volume and structural ordering of synthesized materials (Fig. 1, 3, Table 2).

# CONCLUSIONS

In the present work, the influence of azo dye additives on the hexagonally ordered mesoporous structure of aminosilica materials was studied by low-temperature nitrogen adsorption-desorption and x-ray diffraction analysis. It was proved that introduction of AY and MR into CTAB-assisted sol-gel reaction medium affects the mesoporous structure of resulting aminosilicas due to their incorporation inside micelles of structure-directing agent. The addition of moderate amounts of azo dye additives in the sol-gel reaction mixture causes an increase of surface area and narrowing of pore size distribution in resulting aminosilicas. In general, azo dye additives as components of structure-directing micelles positively impact the formation of the hexagonally ordered mesoporous structure of MCM-41-type silicas due to the simultaneous interaction with micellar and extra-micellar environment at sol-gel synthesis. The results presented in this article expand the possibilities for the synthesis of aminosilica materials with improved structural characteristics using dye enriched aqueous solutions.

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# GLYCOLYZED PRODUCTS FROM PET WASTE AND THEIR CHARACTERIZATION

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#### ABSTRACT

Human needs are an important part of human nature. In parallel with the increasing world population and developing technology, these needs have diversified. To meet some of these needs, new materials, products, techniques, and technologies have been developed over the years. However, the amount of resources needed to sustain our population exceeds what is available. Therefore, natural resources must be used wisely. Furthermore, the use of them in production and consumption must be reduced. Recycling is one of the best ways in conserving natural resources. In this study, a recycling process was performed using different catalyst. Firstly, waste soft drinks bottles (made of PET) were collected. Their caps and labels were removed. They washed with soap and methanol for removing adhesive materials on them. They then cut into approximately 1 cm<sup>2</sup> pieces (flake). Secondly, PET flakes depolymerised by glycolysis with different molar ratio of glycol (propylene glycol (PG), triethylene glycol (TEG), and polyethylene glycol (PEG 400)), in the presence of two different catalyst (zinc acetate and zinc sulphate). And lastly, the obtained product of glycolysis (i.e. polyol, the raw material of polyurethane) was characterized by hydroxyl value (HV) determinations. The effects of catalyst type, glycol type, and glycol amount on the obtained polyol structures were investigated.

Keywords: PET waste, Glycolysis, Polyol, Recycling, Feedstock

# **INTRODUCTION**

Poly (ethylene terephthalate) (PET) is generally used in the packaging of water, beverage and oil bottles. Due to its lightness and durableness, their usage area is gradually expanding. About 4% of the petroleum produced in the world is used in plastic production and approximately 5.75 million tons of this is PET. Its density is 1.33-1.38 g/cm<sup>3</sup>. It is one of the most used plastics with medium hardness. PET is a clear or slightly colored translucent plastic with a high melting temperature of 250 °C. PET burns fast, its flames are colorless [1]. PET is polyester which can degrade in the presence of some reagents, such as water (hydrolysis), alcohols (alcoholysis), acids (acidolysis), glycols (glycolysis) and amines (aminolysis). Among these methods glycolysis is the most commonly used method. In the glycolysis method, the PET product is depolymerized by the glycolysis decomposition process and is separated into its oligomers, bi-hydroxyl ethylene terephthalate (BHET). A large variety of polyols are used in the production of polyurethanes. The glycolysis reaction is the molecular degradation of PET polymer by glycols, in the presence of trans-esterification catalysts, mainly metal acetates [2], various chloride catalyst [3], sodium sulfate [4], where ester linkages are cloven and replaced with hydroxyl terminals [5]. The glycolysis products were used for the synthesis of epoxy resins [6, 7], unsaturated polyester resin [8, 9], alkyd resins [10, 11], polyurethane dispersions [2], melamine formaldehyde resins [12], textile dyes and softeners in textile finishing [3, 4]. The polyols obtained by way of glycolysis of PET have been increasingly used due to the possibility of obtaining products with different molar weights and physical characteristics as a function of the glycol content, the stoichiometric ratio of reagents, and the reaction conditions [13].

This study involves the recycling of waste plastic bottles (PET) and the examination of the polyols obtained by glycolysis process. The effects of catalyst type, glycol type, and glycol amount on the obtained polyol structures were investigated.

# **EXPERIMENTAL SETUP**

Waste soft drinks bottles (made of PET) were collected. Their caps and labels were removed. They washed with soap and methanol for removing adhesive materials on them. They then cut into approximately 1 cm<sup>2</sup> pieces (flake). Secondly, PET flakes depolymerised by glycolysis with different molar ratio of glycol (propylene glycol (PG), triethylene glycol (TEG), and polyethylene glycol (PEG 400)), in the presence of two different catalyst (zinc acetate and zinc sulphate).

Firstly 20 g of PET waste was added to 17.72 g PG, 34.61 g TEG, and 92.30 g PEG; Then by changing the amount of glycol, 20 g of PET waste was added to 79.22 g PG, 150 g TEG, and 434.6 g PEG, such that the Two different catalysts were used for each sample; zinc acetate and zinc sulphate. Zinc acetate is generally used as transesterification catalyst in the glycolysis process. In this study, zinc sulphate which is a lot cheaper than zinc acetate was also used as a catalyst. The above-mentioned mixtures and 0.5 wt% zinc acetate/zinc sulphate, respectively, were charged to a reactor which was fitted with stirrer, reflux condenser, nitrogen inlet, and temperature controller. These were heated at 210 °C for 2 h. The obtained glycolyzed oligoester polyols were analyzed by the hydroxyl value (HV) determination according to the conventional phthalic anhydride/pyridine method. The sample is acetylated with acetic anhydride in presence of pyridine. The hydroxyl value (HV) indicates the necessary amount of KOH (in mg) to neutralize the consummated amount of acetic acid of 1 g fat during acetylation. Each hydroxyl group creates one mole acetic acid, the excessive phthalic anhydride delivers two mole acetic acid. The consumption of acetic acid is determined titrimetric by the difference between main and blind value, which has to be determined parallel. Acetylation solution was prepared by dissolving 28 g of phthalic anhydride in 200 ml of pyridine. About 2 g of sample were accurately weighed by an analytical balance (SHIMADZU AUX320) and added to 25 ml acetylating solution in glass reactor. The reactor was fitted with a reflux condenser and stirred during heating in a boiling water bath for 2 h. Then, reaction mixture was hydrolyzed by 5 ml distilled water and mixture was cooled to room temperature. Finally, the solutions were titrated against 0.5 M KOH standard using phenolphthalein as indicator. A blank run, without the sample (25 ml acetylating solution), was also performed.

# METHODOLOGY

The hydroxyl numbers of the obtained polyols ( $N_{OH}$ ) were determined according to ASTM D4662-03. It is calculated as

$$N_{OH} = \frac{(V_2 - V_1) \cdot N \cdot 56.1}{m_1} + AS, \qquad (1)$$

where  $V_1$  is the sample titer (ml),  $V_2$  is the blank titer (ml),  $m_1$  is the amount of sample (g), AS is the acid number (mg KOH/g), and N is the normality of sodium hydroxide. The AS is calculated as

$$AS = \frac{V_3 \cdot N \cdot 56.1}{m_2},$$
 (2)

where  $V_3$  is the sample titer without phthalic anhydride (ml) and  $m_2$  is the amount of sample without phthalic anhydride (g).

#### **RESULTS AND DISCUSSION**

Hydroxyl numbers of polyols ( $N_{OH}$ ) obtained from different glycols and different mole ratios are given in Figs. 1 and 2. The results show that different  $N_{OH}$  values are obtained with different glycols. Although  $N_{OH}$  does not mean anything by itself, it is an important parameter in polyol characterization. Commercially, it is required to have values between 250 and 500. However, it is predicted that many of the samples recycled with this method used can be used for commercial purposes.



Fig. 1 and 2 show the changes of  $N_{OH}$  with PET/glycol molar ratio of 1:2 and 1:10, respectively. It is clear from the figures that PET can be glycolyzed by PG, TEG, and PEG. However, using different catalyst did not cause a significant change in reaction. It is seen from figures that the hydroxyl number ranges between 160 and 400. As the PET/glycol molar ratio increased, the hydroxyl number decreased. The highest hydroxyl number values were reached in the samples with PG.

Hydroxyl number values may differ according to usage areas. If obtained polyols have hydroxyl numbers of 400 or above, rigid foams, hydroxyl numbers below 400, flexible foams, and hydroxyl numbers below 250, polyurethane adhesives can be obtained. The highest hydroxyl number value was obtained in studies with propylene glycol. Zinc sulphate used as a different catalyst showed similarities with the studies that zinc acetate used in the conventional method. This result indicates that the cheaper zinc acetate can be used in many studies.

# CONCLUSIONS

The main purpose of this study is investigations on the possibility for using glycolysis products of waste PET in commercial use and to eliminate the damage and pollution caused by waste PET bottles. Waste PET flakes were depolymerized by using different molar ratio PET/propylene glycol (PG), triethylene glycol (TEG) and poly(ethylene glycol)(PEG 400) as (1:2 and 1:10). The effects of catalyst, glycol type and the different mole ratios of PET to glycol on hydroxyl numbers have been described. The hydroxyl number obtained as a result of the study showed that it can be used as a raw material in commercial use.

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# **CONFERENCE PAPERS**

# **III.3.** Sustainable Pest Management

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# THE IMPACT OF SOWING TIME AND SEEDING RATE ON THE OCCURRENCE OF LEAF DISEASES IN SPRING WHEAT

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#### ABSTRACT

Local and global climate conditions continue to shift and affect agricultural productivity. Climate change affects crop yields, both directly through changes in plant growth and production and indirectly through impacts on crop diseases. Climate change models are now readily available for a series of standard climate change scenarios and anthropogenic factors and are recognized as very important. As an example, changing sowing and/or harvest dates of crops can be an effective and low-cost option for rendering the crop less vulnerable to pests and diseases. However, the change of planting and/or harvesting dates is dependent on the cultivar, tillage conditions and the region. Improvement of crop protection strategies and tools in line with new requirements to reduce pesticide use will require diverse, flexible and resilient crop production systems that can cope more readily with conditions in the changing environment. This study is focused on low-cost and environment-safe disease management in spring wheat through the choice of sowing date and seeding rate. These factors need to be comprehensively explored to reduce the vulnerability of crop production to climate change.

A multifactor field experiment was carried out at the experimental field of Institute of Agriculture of Lithuanian Research Centre for Agriculture and Forestry in 2020. Three seeding rates (400, 500 and 600 viable seeds m<sup>-2</sup>) and two sowing times (early and optimal) were tested. Powdery mildew (*Blumeria graminis*), septoria leaf blotch (*Zymoseptoria tritici*) and tan spot (*Pyrenophora tritici-repentis*) occurred in spring wheat. Disease assessments were done according to the methods described in European and Mediterranean Plant Protection Organization (EPPO) standard.

Results of the study suggest that the severity of powdery mildew increased in line with the delay of sowing, while seeding rate did not significantly impact the prevalence of disease in the first year of study. Meanwhile a decrease of the severity of septoria leaf blotch was recorded when sowing time was delayed. Increasing of seeding rate resulted in lower prevalence of this disease. The delay of sowing increased the severity of tan spot, while seeding rate did not have significant impact on the severity of this disease. The grain yield was significantly ( $p \le 0.05$ ) affected by the sowing date and seeding rate.

Keywords: spring wheat, sowing time, seed seeding rate, diseases, yield

# **INTRODUCTION**

Wheat (*Triticum aestivum*) is one of the main grain food sources for human consumption, and globally is cultivated in regions of diverse climate, soil type, and latitudes [1]. According to Lithuanian statistics department, spring wheat was the second most popular agricultural cereal crop in 2020.

Global average temperature has increased over the last few decades, and the trend is predicted to continue [2]. Temperature is a major factor affecting crop growth and development, and therefore even a moderate increase in air temperature is likely to influence wheat yield [3, 4] and grain quality [5, 6]. Increased temperatures may affect the fitness of a pathogen population, which could increase or decrease disease infestation in wheat [7].

The global atmospheric carbon dioxide  $(CO^2)$  concentration increased from 284 ppm to 397 ppm between 1832 and 2013 [8]. Such an increase is likely to affect crop plants and the biology of associated pests [9]. Wheat is affected by hundreds of fungal, bacterial and viral pathogens, which cause diseases of varying severity [10]. Wheat pathogens vary in regard to

optimal and conducive environmental conditions; some are active at freezing temperatures, while others cause diseases at temperatures to 35  $^{0}$ C [11, 12].

Continuous monitoring of changes in climate is therefore important for development of management strategies for diseases in the future [13].

Wheat is affected by several diseases across the globe. The most economically important wheat leaf diseases that constitute a major constraint to wheat production globally are septoria leaf blotch (caused by *Zymoseptoria tritici*), tan spot (caused by *Pyrenophora triticirepentis*) [14, 15, 16, 17] and powdery mildew (caused by *Blumeria graminis*) [15, 16, 18].

Septoria leaf blotch (SLB) caused by the ascomycete pathogen *Zymoseptoria tritici* (teleomorph: *Mycosphaerella graminicola*) is a major disease in many wheat growing areas. In Western Europe severe attacks of SLB can result in yield losses of up to 10-30 % [18]. The disease infection can be partly controlled by cultural practices such as growing resistant cultivars, seeding rate, and delayed drilling, minimising infection pressure [19, 20].

Tan spot is a major problem throughout the world where winter and spring wheats are grown [21, 22]. There are reports of a wide spread of the disease in Europe, Southwest Asia, Central Asia, North and South America, Africa, Australia [23, 24, 25, 26, 27, 28].

Powdery mildew, a fungal disease has a serious impact on wheat production. Loss of resistance in cultivars prompts a continuing search for new sources of resistance [29].

Early and accurate detection and diagnosis of plant diseases are key factors in wheat production and for reduction of both qualitative and quantitative losses in crop yield [30].

The study aimed to assess the impact of sowing time and seeding rate of spring wheat on the severity of diseases.

# METHODOLOGY

A multifactor field experiment was carried out at the experimental field of Institute of Agriculture of Lithuanian Research Centre for Agriculture and Forestry in 2020 in Kédainiai district.

The trials were established in the spring wheat cv. 'Flippen'. The previous crop was peas. The weed and pest control and fertilisation were carried out according to standard agronomic practices.

Factor 1: sowing date:

- early sowing date (9<sup>th</sup> of April)
- optimal sowing date (24<sup>th</sup> of April)

Factor 2: seeding rate (400, 500 and 600 seeds  $m^{-2}$ ).

The assessments of powdery mildew (*Blumeria graminis*), septoria leaf blotch (*Zymoseptoria tritici*) and tan spot (*Pyrenophora tritici-repentis*) were done according to the methods described in the European and Mediterranean Plant Protection Organization (EPPO) standard at 75–77 BBCH. The diseased leaf area was visually assessed on the first and second leaves of 10 randomly selected main tillers per plot. Disease assessments were performed on the background of natural infection. Spring wheat was harvested with a small plot combine Wintersteiger Classic Plus when the grain was ripe (BBCH 89). A thousand seed weight was determined by an electronic seed counter (Contador, Pfeuffer GMBH, Germany). The hectolitre weight (HLW) was determined with an Infratec 1241 (Foss) grain analyser.

The experiment was laid out in a completely randomized design with four replications in two blocks. The plot size was 10 m x 1.5 m.

The data of average grain yield, 1000 seed weight and hectolitre weight were analysed by the factorial analysis of variance (ANOVA) The significance of data was determined by Fisher's least significant difference (LSD) test with a significance level of  $p \le 0.05$ . Duncan's test was used to compare the means of disease severity.
# RESULTS

The severity of powdery mildew was much lower in the plots sown at an early date (9<sup>th</sup> of April) compared with the plots sown at an optimal date (24<sup>th</sup> of April) (Fig. 1). The disease severity on the two upper leaves in the early sown plots at different seeding rates was as low as 1.35–3.23 %, while in the plots sown at optimal time it was 8.35–13.13 %. In both early sown and optimal-time sown plots powdery mildew severity on flag leaves was similar, but second leaves were significantly less affected in the plots sown at the highest seeding rate (600 seeds m<sup>-2</sup>) compared with the plots sown at the lowest seeding rate (400 seeds m<sup>-2</sup>).



Fig. 1. The effect of sowing time and seeding rate on powdery mildew (*Blumeria graminis*) severity in spring wheat at 75–77 BBCH. Columns with the same letters do not differ at  $p \le 0.05$ 

In 2020, septoria leaf blotch infection in spring wheat was severe. At BBCH 75–77, in early sown plots the disease severity on both flag and second leaves was sightly higher than in the plots sown at optimal time (Fig. 2). The trend of increase of septoria leaf blotch severity on the flag and second leaves in the plots sown at the lowest seeding rate (400 seeds  $m^{-2}$ ) in both early sown plots and those sown at optimal time was observed.





The tan spot infection in the plots sown at optimal time was much higher compared with the early sown plots (Fig. 3). The disease severity in the early sown plots was 9.50–13.25 %, while in the plots sown at optimal time it was 18.88–25 %. The severity of the disease on flag and second leaves did not differ significantly between the plots sown at the early date and optimal date.



Fig. 3. The effect of sowing time and seeding rate on tan spot (*Pyrenophora tritici-repentis*) severity in spring wheat at 75–77 BBCH. Columns with the same letters do not differ at  $p \le 0.05$ 

The green leaf area of flag leaves in the plots sown at optimal time at different seeding rates practically did not differ (Fig. 4). In early sown plots, the trend of the increase of green leaf area at all tested seeding rates, especially in the plots sown at 500 seeds  $m^{-2}$  was noticed.



Fig. 4. The effect of sowing time and seeding rate on green leaf area in spring wheat. Columns with the same letters do not differ at  $p \le 0.05$ 

The yield of spring wheat in early sown plots was significant higher compared with the plots sown at optimal time (Table 1). Statistical analysis revealed the relationship between the time of sowing and seeding rate ( $p \le 0.05$ ).

Seeding rate (B)	Sowing	time (A)
	Early	Optimal
400 seeds $m^{-2}$	7.39c	6.21b
500 seeds $m^{-2}$	7.34c	6.17b
$600 \text{ seeds } \text{m}^{-2}$	7.54c	5.91a

Table 1. The effect of spring wheat sowing time and seeding rate on grain yield (t ha<sup>-1</sup>)

Values followed by different letters are significantly different ( $p \le 0.05$ ) based on Fisher's LSD test

Evaluation of 1000 grain weight in terms of sowing time and seeding rate did not show a relationship between factors A and B (Table 2). The trend of thousand grain weight decrease at the highest seeding rate in early sown plots was noticed.

Table 2. The effect of spring wheat sowing time and seeding rate on 1000 grain weight (g)

Seeding rate (B)	Sowing	time (A)
	Early	Optimal
400 seeds $m^{-2}$	36.42ab	36.08ab
500 seeds $m^{-2}$	36.91b	35.87a
600 seeds m <sup>-2</sup>	35.55a	35.82a

Values followed by different letters are significantly different ( $p \le 0.05$ ) based on Fisher's LSD test

Evaluation of hectolitre weight (HLW) did not show a relationship between the sowing time and seeding rate (Table 3). The highest HLW was in early sown plots at a seeding rate of 600 seeds  $m^{-2}$ . Analysis of HLW showed equal values between the least dense crops (sown at 400 seeds  $m^{-2}$ ) and most dense crops (sown at 600 seeds  $m^{-2}$ ).

Table 3. The effect of spring wheat sowing time and seeding rate on hectolitre weight (HLW)

Seeding rate (B)	Sowing	time (A)
	Early	Optimal
400 seeds $m^{-2}$	75.53b	75.33ab
500 seeds $m^{-2}$	75.18ab	74.53a
600 seeds m <sup>-2</sup>	75.80b	75.33ab

Values followed by different letters are significantly different ( $p \le 0.05$ ) based on Fisher's LSD test

#### DISCUSSIONS

Disease severity is dependent on many factors, including cultural practices [31], variation in the weather conditions [32] and the level of cultivar susceptibility [33, 34, 35, 36]. The results of the first-year study suggest that the severity of powdery mildew in spring wheat increased in line with the delay in sowing.

Since the early 1980s, septoria leaf blotch has taken over and is now regarded as the most important disease in wheat [37] with yield losses in the range of 10–50% depending on the region and yearly disease pressure [38]. Some authors suggest that the disease can partly be controlled by cultural practices such as growing resistant cultivars, seed rate, and delayed drilling, minimizing infection pressure [19, 39]. Several agronomic practices, e.g., late sowing and planting of resistant cultivars [40, 19, 41] have shown some potential keeping the disease levels low and minimising epidemics [38]. Late sowing can decrease the disease levels and the epidemic is generally delayed in winter wheat crop [42]. Our results in spring wheat also showed a decrease in the severity of septoria leaf blotch when sowing time had been delayed.

In Latvia and Lithuania, tan spot was noticed and identified in the first half of the 1990s [43]. The findings of Ronis and Semaškienė [44] suggest that the severity of leaf spot diseases

depends mainly on the weather conditions and resistance level of the studied varieties. Our study results indicate that the severity of tan spot increased in line with the delay in sowing.

Previous regional studies showed that the prevalence of wheat diseases varies across the European region [45]. The variation is related to the interaction between the disease cycles and climatic conditions, susceptibility of the major cultivars, cultivation history and cropping practices, including sowing time and tillage [46].

To minimize yield or productive tiller losses due to diseases in min-tillage system, researchers recommend increasing seeding rate [47]. Our first-year results showed that spring wheat sown at the highest seeding rate of 600 seeds  $m^2$  at an early sowing time produced higher grain yield than that sown at optimal sowing time.

Severely diseased leaves eventually wilt and die prematurely [48]. The results of oneyear study indicated a positive influence of early sowing time on spring wheat green leaf area.

As a consequence of the complexity of the agricultural system, where plants and diseases are not the only components, there cannot be one simple relationship between the disease severity and yield. The same disease severity may result in very different yield losses from one year to another: among other factors, the length of the ripening period, the defoliation experienced, and the cultivar's tolerance of leaf blotch might influence the impact on yield [49, 50].

# CONCLUSIONS

The results of the study suggest that the severity of powdery mildew was lower in the plots shown at the early date compared with those sown at the optimal date. The trend of increase of septoria leaf blotch severity in the plots sown at the lowest seeding rate (400 seeds  $m^{-2}$ ) in both early and optimal time-sown plots was observed. Increasing of seeding rate resulted in lower prevalence of this disease. Tan spot infection in the plots sown at optimal time was much higher than in the early sown plots. In early sown plots the trend of the increase of green leaf area at all tested seeding rates was noticed.

The yield of spring wheat in early sown plots was significant higher compared to the plots shown at an optimal time. Statistical analysis revealed the relationship between the sowing time and seeding rate ( $p \le 0.05$ ). The trend of a thousand grain weight decrease at the highest seeding rate in early sown plots was noticed. An analysis of hectolitre weight showed equal values between the seeding rates of 400 and 600 seeds m<sup>-2</sup>.

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# CARROTS DISEASES CONTROL BY ESSENTIAL OILS

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#### EXTENDED ABSTRACT

#### **OVERVIEW**

Heavy losses in economically valuable horticultural plant yield are usually caused by the dothideomycetes fungal pathogens of the genus Alternaria, which have a broad host range, include endophytic, saprobic and pathogenic species linked with a wide variety of substrates, and are well adapted to unfavourable environmental conditions [1]. Carrots as hosts are one of the most valuable in nutrients vegetables, but most often vulnerable plants because of Alternaria leaf blight and black rot damage to their commercial appearance or the loss of foliage [2]. Chemical plant protection is the primary tool in pathogen maintenance because of its favourable price and effective usage. However, fungicide resistance, consumer health concerns, and environmental pollution have become significant drawbacks of conventional fungicide use [3]. Therefore, alternatives to chemical plant protection are currently being sought. Compounds extracted from plants and biological control agents are increasingly used for plant protection [4]. Studies on Origanum vulgare subsp. vulgare and Origanum vulgare subsp. hirtum efficiency against some fungi of the genus Aspergillus, Candida and Fusarium, and also some bacteria can be found in the literature [5, 6]. According to the potential of essential oils derived from spices to maintain food products [7], there is an increase in research dealing with the control of carrots diseases caused by Alternaria species [8]. Therefore, the current study was aimed to evaluate the ability of the Origanum vulgare subsp. vulgare and Origanum vulgare subsp. hirtum essential oils to control Alternaria spp. growth.

#### METHODS

The research was carried out at the LAMMC Institute of Horticulture in Lithuania in 2019 - 2020. Isolation from infected carrot tissues was performed to obtain *Alternaria* single-spore isolates. These isolates were cultured on potato dextrose agar (PDA) at  $25 \pm 2$  °C in the dark for 7 days and identified by morphological traits typical of the colonies [9, 10]. The essential oils of *Origanum vulgare* subsp. *vulgare* and *Origanum vulgare* subsp. *hirtum* were extracted by hydro-distillation from local dried material and tested at different concentrations.  $200 \ \mu L \ L^{-1}$ ,  $400 \ \mu L \ L^{-1}$  and  $600 \ \mu L \ L^{-1}$  of pure essential oil were mixed with 45 °C PDA. Petri plates inoculation was with 5 mm *Alternaria* mycelial plugs placed in the middle of the Petri dishes. Plates were incubated at  $25 \pm 2$  °C in the dark. The control treatments were oil-free. The diameter (mm) of *Alternaria* spp. colony growth diameter was used for radial colony growth calculations [11].

#### RESULTS

Moving towards a more sustainable food production, interest in essential oils is growing because of their biodegradable and ecological properties. For our study, we selected *Origanum vulgare* subsp. *vulgare* and *Origanum vulgare* subsp. *hirtum* essential oils and evaluated their efficiency on *Alternaria* spp. growth control. The assay revealed that the investigated essential oils had a moderate ability to control pathogens of the genus *Alternaria*. The effect of different concentrations of *O. vulgare* subsp. *hirtum* essential oil was inconsistent throughout the experiment. Nevertheless, 400  $\mu$ L L<sup>-1</sup> showed the most potent antifungal activity. In an investigation conducted by Askun et al. [5], methanol extract of this plant significantly inhibited the mycelial growth of some fungi of the genus *Aspergillus, Candida* and *Fusarium*. In our research, suppression of mycelial growth increased with *O. vulgare* subsp. *vulgare* 

*essential oil.* Treatment with 600  $\mu$ L L<sup>-1</sup> showed the best antifungal activity against pathogen and had significant differences from the control 1, 2, 3 and 7 days after inoculation. Sarikurkcukcu et al. [6] reported that *O. vulgare* subsp. *vulgare* essential oil showed stronger antimicrobial activity comparing to *O. vulgare* subsp. *hirtum against some bacterial strains*.

#### CONCLUSIONS

The antifungal properties of the studied essential oils proved to be not equal. The best results were obtained with the *Origanum vulgare* subsp. *vulgare* essential oil concentration of 600  $\mu$ L L<sup>-1</sup> and with the *Origanum vulgare* subsp. *hirtum* – 400  $\mu$ L L<sup>-1</sup>. The results confirm the antifungal effect of these essential oils, but higher concentrations should be tested in the future.

Keywords: Plant protection, Alternaria spp., oregano, vegetable

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# EFFECT OF HILLY RELIEF ON THE INCIDENCE OF WEEDS IN THE CROPS OF SPRING BARLEY

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#### ABSTRACT

The experiment was carried out at the Vezaiciai Branch of the Lithuanian Research Centre for Agriculture and Forestry on the hilly topography of Zemaiciai Highland (latitude 55°577' N, longitude 22°482' E, 185.0 m above sea level). The southern exposition slope's soil was slightly eroded *Eutric Retisol (loamic) (RT-eu.lo)* the steepness of the slope was 9-11°. The aim of the study was to investigate the impact of hilly relief on weed number, weed agrobiological groups and soil seed bank changes in the crops of spring barley. The study included different parts of the hill (summit, midslope and footslope).

The weed number (I and II assessment) and weed dry matter mass (DM) (II assessment) in the summit of the hill were determined to be greater, respectively: by 1.5-1.6, 1.7-1.8 and 1.6-2.4 times compared to other parts of the hill. Under conditions of hilly relief in the beginning of plant growing season, the least number (4764 seeds m<sup>-2</sup>) of the vital weed seeds in permanent soil seed bank was determined to be in the summit of the hill compared to the midslope and footslope. In the soil of midslope and footslope, the number of weed seeds was respectively 2.5 and 2.2 times greater than in the summit. The same amount of weed seeds was determined in all parts of the hill both in 0-5 and 5-15 cm depths of the soil. In the end of plant growing season in the soil of spring barley crops, the number of weed seeds was determined to the beginning of growing season. 75.6-79.0 % of the weed seeds were found in the depth of 0-5 cm. The soil in the summit of the hill was the most contaminated with weed seeds (43377 seeds m<sup>-2</sup>).

Keywords: hilly relief, spring barley, weed dry matter mass, weed number, soil seed bank, weed groups.

# **INTRODUCTION**

Weeds are mostly not welcomed by a human - they interfere in the soil and grow in cultural crops, while competing with them for the same vital resources - light, water and nutrients. The yield of cultural crops decreases and diminishes in quality because of weeds [1]. The spread of weeds, their biodiversity and development are mostly based on the soil properties that result in different nutritional aspects [2]. The maximum biodiversity in crop rotation (crop diversity), winter and summer crop rotation restrict the reproduction and spread of various typologies of weeds (annual, biennial or perennial) [3;4]. The dynamics of weed contamination relies on the amount of seed bank [5], structure [6] and horizontal distribution [7], as well as on the seed bank distribution in various soil layers [8]. Auškalnienė et al. [9] states that the seed bank of the soil is the main contamination source of annually recurring weeds and makes up the biggest part of weed species composition. The weed seed bank may predict the possible influence of crop yield and quality to the crop weed competition. The weeds compete with the crops for resources; therefore, the loss of crops can amount to 34% [10;11]. There are about 30–40% of weeds that germinated in spring and remained until harvest in the barley crops, depending on the pre-sowing and crop area rotation [12]. The number of weeds and their botanical composition changes depending on relief. The contamination of weeds that are resistant to water shortage and bigger soil acidity are dominant on the summits and midslopes: Scleranthus annuus L., Spergula arvensis L. Weeds that thrive in moisture and richer soil can be found on the footslope: *Chenopodium album* L., *Convolvulus arvensis* L., *Agrostis stolonifera* L. Some weeds grow well in all parts of the slope [13].

The aim of the study was to investigate the impact of hilli relief on weed number, weed groups and soil seed bank changes in spring barley crops.

#### **MATERIALS AND METHODS**

The experiment was carried out at the Vėžaičiai Branch of the Lithuanian Research Centre for Agriculture and Forestry on the midslope soil of Zemaiciai Highland covered by different anti-erosion agrophytocenoses in Kaltinenai. The geographical location of the experiment: latitude 55°577′ N, longitude 22°482′ E, 185,0 m above sea level. The steepness of the slope was 9–11°. The soil of the southern exposition slope was slightly eroded Eutric Retisol (loamic) (RT-eu.lo). Soil agrochemical and physical properties are presented in Table 1.

	Parts of the hill						
Soil properties	sum	nmit	mids	slope	footslope		
	0-5 cm	5-15 cm	0-5 cm	5-15 cm	0-5 cm	5-15 cm	
Soil pH <sub>KC1</sub>	5.6±0.12	5.4±0.13	5.3±0.04	5.1±0.17	5.1±0.08	5.1±0.09	
Mobile P <sub>2</sub> O <sub>5</sub> mg kg <sup>-1</sup>	$192 \pm 28.87$	201±12.45	165±6.33	$168 \pm 15.60$	$149 \pm 5.84$	$148 \pm 8.35$	
Mobile K <sub>2</sub> O mg kg <sup>-1</sup>	209±5.13	$112 \pm 4.04$	$198 \pm 4.51$	98±9.06	223±31.1	107±9.96	
N <sub>total</sub> , %	$0.078 \pm 0.00$	$0.077 \pm 0.00$	$0.097 \pm 0.00$	$0.096 \pm 0.00$	$0.106 \pm 0.00$	$0.101 \pm 0.00$	
Corg	$0.9\pm0.04$	$0.8\pm0.09$	$1.1\pm0.04$	1.1±0.03	$1.1\pm0.08$	1.1±0.02	
Soil moisture, %	16.08±0.42	14.73±0.06	20.49±0.47	19.45±0.49	21.78±0.21	20.62±0.19	

Table 1. Soil agrochemical characteristics at experiment established in 2020.

mean values  $\pm$  standard deviation

Anti-erosion barley-weed crop rotation was used for the research, where the second crop rotation plant – spring barley was used in 2020. Stubble was left during winter season to preserve the slope's soil from erosion, and minimal soil cultivation was carried out in the spring. Spring barley "Luokė" were sown along the slope with the amount of 220 kg ha<sup>-1</sup>. Mineral fertilization – NPK 9-14-27+7S 250 kg ha<sup>-1</sup> was used after sowing. Spring barley were sprayed with MCPA 500 g l<sup>-1</sup> during the stem elongation stage (BBCH 32) with the norm of 0.5 l ha<sup>-1</sup> (MCPA Super) and tritosulfuron 25% + dicamba 50%, norm 0.17 kg ha<sup>-1</sup> (Arrat).

The hill slope used for the research was 65 meters long. The research land lane was 3,2 meters wide.

For plant and soil seed bank sampling stationary 21 m<sup>-2</sup> square plot  $7\times3$  m has been arranged in each part of the hill. Each model plot was split into 3 rectangular shapes that replicate ( $7\times1$  m) 7 m<sup>2</sup>. Distances between model plots in different parts of the hill were 15 meters.

Weed assessment was performed in stationary fields of 0.25 m<sup>-2</sup> size in six positions of every plot during the heading of spring barley crops (BBCH 58) and ripening (BBCH 86) phases. During the first assessment, weed species composition was determined, during the second assessment weed species composition and dry matter mass (DM) were determined. Weed number was recalculated unit per m<sup>-2</sup> and dry matter mass – g m<sup>-2</sup>.

The viable seed bank (0 to 5 and 5 to 15 cm depths) was estimated from soil samples taken in spring and autumn of 2020. Soil contamination with weed seeds was investigated in the depths of 0 to 5 cm and 5 to 15 cm, 2 kg of soil from 20 positions in each model plot were collected using an agrochemical drill. The soil was dried out. Totally five 100 g samples were taken out of 2 kg soil sample and weighed. Later, the soil samples were wet-sieved through a 0.25 mm sieve until all contents of the soil were washed out. Remained mineral part of the soil

was separated from the organic part and weed seeds using the saturated salt solution. Weed seeds were identified using binoculars with  $8.75 \times$  magnification. Weed seed species were determined by Grigas [14]. Weed seed number was recalculated to thousands of unit m<sup>-2</sup>.

Soil agrochemical characteristics were determined from the soil samples taken from 0 to 5 and 5 to 15 cm depths before establishing the experiment. Soil  $pH_{KCL}$  was determined in 1 M KCl soil sample extracts using a digital pH-meter, mobile  $P_2O_5$  and  $K_2O$  – using the Egner-Riehm-Domingo (A-L) method, total nitrogen – by Kjeldahl (ISO 11261:1995). Soil bulk density was determined from a core sample by the Katchinski method, soil moisture content was determined by weight method. Soil texture was determined by the Fere triangle (FAO recommended method) according to the percentage of sand, silt and clay fractions in the graphical diagram.

The ANOVA (analysis of variance) and the least significant difference (LSD) methods were employed. To achieve the homogeneity of variance, the data were (Sqr (x + 1)) transformed.

# RESULTS

#### The number of weeds in the spring barley crops

Ever since the plants were planted for germination, growing and development under the conditions of a hilly relief, they were exposed to different environments [15;16], because in the lower parts of the slopes, with bigger physical amount of clay and mud, as other authors indicate, the moisture resources become higher, the amount of humus and nutrients increase, while the acidity decreases (Table 1). Due to uneven moisture, acidity and amount of nutrients in the soil, the environment for the growth and development of spring barley crops were diverse, which lead to changes to the indicators of weediness of crops.

During the heading stage of spring barleys (BBCH 58) significantly more (1.5 times) weeds were found on the summit of the hill than on the midslope or footslope. A considerable impact was due to spring barley development. Annual dicotyledonous, perennial monocotyledonous and *Equisetum arvense* L. accounted for 10.4% of the total amount of weeds on the summit of the hill. *Agropyron repens* L. made up 61% of all weeds on the slope of the hill, an average of 160.67 weeds m<sup>-2</sup>. *Spergula arvensis* L. (52 weeds m<sup>-2</sup>), *Viola arvensis* Murr. (15.33 weeds m<sup>-2</sup>), *Polygonum bistorta* L. (2.67 weeds m<sup>-2</sup>), *Fallopia convolvulus* L. (5.33 weeds m<sup>-2</sup>) and *Chenopodium album* L. (0.67 weeds m<sup>-2</sup>) were found on the slope of the hill from the range of annual dicotyledonous. *Equisetum arvense* L. accounted for 10% of all weeds located on the slope of the hill (26.67 weeds m<sup>-2</sup>.) (Tables 2 and 3).

			Parts of	the hill		
Weeds	Su	mmit	Midslope		Footslope	
	BBCH	BBCH	BBCH	BBCH	BBCH	BBCH
	58	86	58	86	58	86
	An	nual dicotyle	donous			
Spergula arvensis L.	52	13.33	10	-	19.33	-
		4.85				
Viola arvensis Murr.	15.33	<u>49.33</u>	56.67	<u>52</u>	32.67	24.67
		5.51		19.6		4.52
Polygonum aviculare L.	-	<u>1.33</u>	-	-	-	-
		0.13				
Veronica chamaedrys L.	-	<u>0.67</u>	-	<u>33.3</u>	-	<u>20.67</u>

Table 2. The number of weeds and their mass in the spring barley crops, weeds m<sup>-2</sup> / g m<sup>-2</sup> Avarage experiment data. Kaltinėnai 2020

		0.07		4 06		2.05
Polygonum historta L	2.67	-	4	2	2.67	-
i orygoniani orstorita E.	2.07		•	$\frac{2}{119}$	2.07	
Leonurus cardiaca I	_	_	_	0.67	_	33
Leonaras curataca L.		_	_	$\frac{0.07}{0.03}$	_	<u> </u>
Galeonsis tetrahit I	_		_	0.67		1.25
Outeopsis tetrunti L.		_	-	$\frac{0.07}{0.23}$	_	_
Fallonia convolvulus I	5 33		4 67	0.23	1	_
Futiopia convoivatas L.	5.55	_	4.07	-	-	_
Chananadium album I	0.67					
Chenopolatam atoum L.	0.07	-	-	-	-	-
Triplaurosparmum			0.67		0.67	
n aufonatum I	-	-	0.07	-	0.07	-
perjoratum L.						
Cancella hursa nastoria I					0.67	
Capsella bursa-pasions L.	-	-	-	-	0.07	-
	1	al monoactur	ladanaya			
De a succes I	Annu			210	70	122 67
Poa annua L.	-	$\frac{23.3}{0.64}$	04	$\frac{518}{2612}$	70	432.07
		0.64		36.12		45.49
Echinochloa crus-galli L.	-	<u>791.3</u>	-	<u>85.3</u>	-	<u>30.67</u>
		92.39		21.2		8.25
		0.00.0.6	1 10 01	100.01	120.01	<b>7</b> 11.00
In total annual	76	<u>879.26</u>	140.01	<u>489.94</u>	130.01	<u>511.98</u>
In total annual	76	<u>879.26</u> 103.59	140.01	<u>489.94</u> 82.43	130.01	<u>511.98</u> 61.56
In total annual	76 Pere	<u>879.26</u> 103.59 nnial dicotyle	140.01 edonous	<u>489.94</u> 82.43	130.01	<u>511.98</u> 61.56
In total annual Sonchus arvensis L.	76 Pere -	879.26 103.59 nnial dicotyle <u>0.67</u>	140.01 edonous -	<u>489.94</u> 82.43	-	<u>511.98</u> 61.56 <u>1.33</u>
In total annual Sonchus arvensis L.	76 Pere	879.26 103.59 nnial dicotyle <u>0.67</u> 0.3	140.01 edonous -	<u>489.94</u> 82.43	-	<u>511.98</u> 61.56 <u>1.33</u> 0.16
In total annual Sonchus arvensis L. Leontodon autumnalis L.	76 Pere - -	879.26 103.59 nnial dicotyle <u>0.67</u> 0.3 -	140.01 edonous - -	<u>489.94</u> 82.43 - <u>0.7</u>	-	<u>511.98</u> 61.56 <u>1.33</u> 0.16 -
In total annual Sonchus arvensis L. Leontodon autumnalis L.	76 Pere - -	879.26 103.59 nnial dicotyle <u>0.67</u> 0.3 -	140.01 edonous - -	<u>489.94</u> 82.43 - <u>0.7</u> 0.74	-	<u>511.98</u> 61.56 <u>1.33</u> 0.16 -
In total annual Sonchus arvensis L. Leontodon autumnalis L. Lamium album L.	76 Pere - -	879.26 103.59 nnial dicotyle <u>0.67</u> 0.3 -	140.01 edonous - - 1.33	<u>489.94</u> 82.43 - <u>0.7</u> 0.74 -	- - 14	<u>511.98</u> 61.56 <u>1.33</u> 0.16 -
In total annual Sonchus arvensis L. Leontodon autumnalis L. Lamium album L.	76 Pere - -	879.26 103.59 nnial dicotyle <u>0.67</u> 0.3 -	140.01 edonous - - 1.33	<u>489.94</u> 82.43 - <u>0.7</u> 0.74 -	- - 14	<u>511.98</u> 61.56 <u>1.33</u> 0.16 -
In total annual Sonchus arvensis L. Leontodon autumnalis L. Lamium album L. Taraxacum officinale L.	76 - - - -	879.26 103.59 nnial dicotyle <u>0.67</u> 0.3 - -	140.01 edonous - - 1.33 -	<u>489.94</u> 82.43 - <u>0.7</u> 0.74 -	- - 14 3.33	<u>511.98</u> 61.56 <u>1.33</u> 0.16 - -
In total annual Sonchus arvensis L. Leontodon autumnalis L. Lamium album L. Taraxacum officinale L.	76 - - - -	879.26 103.59 nnial dicotyle <u>0.67</u> 0.3 - -	140.01 edonous - - 1.33 -	<u>489.94</u> 82.43 - <u>0.7</u> 0.74 -	- - 14 3.33	<u>511.98</u> 61.56 <u>1.33</u> 0.16 - -
In total annual Sonchus arvensis L. Leontodon autumnalis L. Lamium album L. Taraxacum officinale L. Galium aparine L.	76 Pere - - - -	879.26 103.59 nnial dicotyle <u>0.67</u> 0.3 - - -	140.01 edonous - - 1.33 - -	<u>489.94</u> 82.43 - <u>0.7</u> 0.74 - -	- - 14 3.33 1.33	<u>511.98</u> 61.56 <u>1.33</u> 0.16 - - -
In total annual Sonchus arvensis L. Leontodon autumnalis L. Lamium album L. Taraxacum officinale L. Galium aparine L.	76 Pere - - - -	879.26 103.59 nnial dicotyle <u>0.67</u> 0.3 - - -	140.01 edonous - - 1.33 - -	<u>489.94</u> 82.43 - <u>0.7</u> 0.74 - -	- - 14 3.33 1.33	<u>511.98</u> 61.56 <u>1.33</u> 0.16 - - -
In total annual Sonchus arvensis L. Leontodon autumnalis L. Lamium album L. Taraxacum officinale L. Galium aparine L.	76 Pere - - - - Perenr	879.26 103.59 nnial dicotyle <u>0.67</u> 0.3 - - - - nial monocoty	140.01 edonous - - 1.33 - - yledonous	<u>489.94</u> 82.43 - <u>0.7</u> 0.74 - -	- - 14 3.33 1.33	<u>511.98</u> 61.56 <u>1.33</u> 0.16 - - -
In total annual Sonchus arvensis L. Leontodon autumnalis L. Lamium album L. Taraxacum officinale L. Galium aparine L. Agropyron repens L.	76 Pere - - - - Perenr 160.67	879.26 103.59 nnial dicotyle <u>0.67</u> 0.3 - - - - - - - -	140.01 edonous - 1.33 - - yledonous 22	<u>489.94</u> 82.43 - <u>0.7</u> 0.74 - - - <u>1.3</u>	- - 14 3.33 1.33 18.67	<u>511.98</u> 61.56 <u>1.33</u> 0.16 - - - - 4.67
In total annual Sonchus arvensis L. Leontodon autumnalis L. Lamium album L. Taraxacum officinale L. Galium aparine L. Agropyron repens L.	76 Pere - - - - Perenr 160.67	$     \frac{879.26}{103.59} $ nnial dicotyle $     \frac{0.67}{0.3} $ nial monocotyle $     \frac{2}{0.51} $	140.01 edonous - 1.33 - - yledonous 22	<u>489.94</u> 82.43 - <u>0.7</u> 0.74 - - <u>1.3</u> 0.46	- - 14 3.33 1.33 18.67	<u>511.98</u> 61.56 <u>1.33</u> 0.16 - - - <u>-</u> - <u>-</u> <u>4.67</u> 9.22
In total annual Sonchus arvensis L. Leontodon autumnalis L. Lamium album L. Taraxacum officinale L. Galium aparine L. Agropyron repens L.	76 Pere - - - - Perenr 160.67	$     \frac{879.26}{103.59} $ nnial dicotyle $     \frac{0.67}{0.3} $ nial monocotyle $     \frac{2}{0.51} $ Equisetopsi	140.01 edonous - 1.33 - - yledonous 22 da	$     \frac{489.94}{82.43}     -     \frac{0.7}{0.74}     -     -     \frac{1.3}{0.46}   $	- - 14 3.33 1.33 18.67	$     \frac{511.98}{61.56}     \frac{1.33}{0.16}     -     -     -     \frac{-}{-}     \frac{4.67}{9.22}   $
In total annual Sonchus arvensis L. Leontodon autumnalis L. Lamium album L. Taraxacum officinale L. Galium aparine L. Agropyron repens L. Equisetum arvense L.	76 Pere - - - - Perent 160.67	$     \begin{array}{r}         \underline{879.26} \\         \underline{103.59} \\         \underline{103.59} \\         \underline{103.59} \\         \underline{0.67} \\         \underline{0.3} \\         \underline{-} \\$	140.01 edonous - - 1.33 - - yledonous 22 da 1.33	$     \frac{489.94}{82.43}     -     \frac{0.7}{0.74}     -     -     \frac{1.3}{0.46}     2     $	130.01 - - 14 3.33 1.33 18.67 6	<u>511.98</u> 61.56 <u>1.33</u> 0.16 - - - <u>-</u> - <u>-</u> <u>4.67</u> 9.22 10.67
In total annual Sonchus arvensis L. Leontodon autumnalis L. Lamium album L. Taraxacum officinale L. Galium aparine L. Agropyron repens L. Equisetum arvense L.	76 Pere - - - - Perenr 160.67 26.67	$     \begin{array}{r}         \underline{879.26} \\         \underline{103.59} \\         \underline{103.59} \\         \underline{103.59} \\         \underline{0.67} \\         \underline{0.3} \\         \underline{-} \\$	140.01 edonous - 1.33 - - yledonous 22 da 1.33	$     \frac{489.94}{82.43}     -     \frac{0.7}{0.74}     -     -     \frac{1.3}{0.46}     \frac{2}{2.29}   $	130.01         -         -         14         3.33         1.33         18.67         6	$     \frac{511.98}{61.56}     \frac{1.33}{0.16}     - $
In total annual Sonchus arvensis L. Leontodon autumnalis L. Lamium album L. Taraxacum officinale L. Galium aparine L. Agropyron repens L. Equisetum arvense L. In total perennial	76 Pere - - - - Perenr 160.67 26.67 187.34	$     \begin{array}{r}         & \underline{879.26} \\         & 103.59 \\         & 103.59 \\         & \hline 103.59 \\         & \hline 103.59 \\         & \hline 0.67 \\         & 0.3 \\         & \hline - \\         &$	140.01 edonous - - 1.33 - - yledonous 22 da 1.33 24.66	$     \frac{489.94}{82.43}     -     \frac{0.7}{0.74}     -     -     \frac{1.3}{0.46}     \frac{2}{2.29}     4     $	130.01         -         -         14         3.33         1.33         18.67         6         43.33	$     \frac{511.98}{61.56}     \frac{1.33}{0.16}     -     -     -     -     \frac{4.67}{9.22}     \frac{10.67}{7.4}     16.67     $

Note: weeds  $m^{-2}$  in the numerator, g  $m^{-2}$  in the denominator. "-" illustrates that this type of weed was not located.

Table 3. The number of weeds in the spring barley crops in heading stage (BBCH 58), Kaltinėnai 2020

Parts of the hill	Number of weeds, weeds m <sup>-2</sup>			
	In total	Annual	Perennial	
Summit	263.34	76.00	187.34	
Midslope	164.67*	140.01	24.66**	
Footslope	173.34*	130.01	43.33**	
	0 5 0 1 0 0 0 /	1 1 111 1 1		

Note. \*,\*\*: reliable on 95% and 99% probability levels.

Annual weeds were dominant in the midslope and footslope. The most common was *Poa* annua L. (64 and 70 weeds m<sup>-2</sup> respectively). *Viola arvensis* Murr. was prevalent on the midslope 56.67 weeds m<sup>-2</sup> on average and on the footslope – 32.67 weeds m<sup>-2</sup>. *Capsella bursa-* pastoris L. (0.67 weeds m<sup>-2</sup>), *Taraxacum officinale* L. (3.33 weeds m<sup>-2</sup>) and *Galium aparine* L. (1.33 weeds m<sup>-2</sup>) were common only on the footslope. The average amount of *Equisetum* arvense L. found on the midslope and footslope was 1.33 and 6 weeds m<sup>-2</sup>.

Parts of the hill	Number of weeds, weeds m <sup>-2</sup>			Weed DM mass, g m <sup>-2</sup>		
	In total	Annual	Perennial	In total	Annual	Perennial
Summit	897.23	879.26	17.97	125.63	103.59	22.04
Midslope	493.94**	489.94**	4.00	85.92	82.43	3.49
Footslope	528.65**	511.98**	16.67	78.34	61.56	16.78

Table 4. The number of weeds in the spring barley crops in ripening stage (BBCH 86),Kaltinėnai 2020

Note. \*,\*\*: reliable on 95% and 99% reliability levels.

The weeds sprout during the whole vegetation period in the spring barley crops [17]. The amount of weed discovered during the ripening stage (BBCH 86) of spring barley was 3 times bigger than during the heading stage. Echinochloa crus-galli L. accounted for 88% of all the weeds on the summit of the hill, while the Poa annua L. accounted for 64% of all weeds on the midslope and 82% on the footslope. During the second assessment the annual dicotyledonous were most commonly found. Viola arvensis Murr. (24.67–52 weeds m<sup>-2</sup>) was spread out most abundantly out of all annual dicotyledonous in all parts of the hill. The Veronica chamaedrys L. was not as common (0.67–33.3 weeds m<sup>-2</sup>). Spergula arvensis L. (averagely 13.3 weeds m<sup>-2</sup>) <sup>2</sup>) and *Polygonum aviculare* L. (averagely 1.3 weeds m<sup>-2</sup>) were found only on the summit, while Polygonum bistorta L. (averagely 2 weeds m<sup>-2</sup>) and Galeopsis tetrahit L. (averagely 0.67 weeds  $m^{-2}$ ) – on the midslope of the hill. *Leonurus cardiaca* L. (0.67–3.3 weeds  $m^{-2}$ ) was sparsely distributed on the midslope and footslope. Other weed plant species, such as perennial dicotyledonous and perennial monocotyledonous were scarcely distributed, only 0.5% of them out of all the weeds were determined in the second assessment. Perennial weed Equisetum arvense L. (from 2 to 15.3 weeds m<sup>-2</sup> on average) was found on all parts of the hill. A very little amount of Sonchus arvensis L. and Leontodon autumnalis L. were determined out of the perennial dicotyledonous. Agropyron repens L., out of the perennial monocotyledonous, was in all parts of the hill, averaging from 2 to 4.67 weeds m<sup>-2</sup>.

After analyzing the outspread of weeds in the spring barley during the ripening stage (BBCH 86), 1.8 times more weeds were found on the summit of the hill than on the midslope, and 1,7 times more than on the footslope (Table 4). Different weed species were found during both assessments. *Fallopia convolvulus* L., *Chenopodium album* L., *Tripleurospermum perforatum* L., *Capsella bursa-pastoris* L., *Lamium album* L., *Taraxacum officinale* L. and *Galium aparine* L. were discovered in the spring barley during the heading stage, while they were absent during the second assessment. On the contrary, weeds found during the ripening stage of the spring barley (*Polygonum aviculare* L., *Veronica chamaedrys* L., *Leonurus cardiaca* L., *Galeopsis tetrahit* L., *Echinochloa crus-galli* L. *Sonchus arvensis* L. and *Leontodon autumnalis* L.), were absent during the heading stage (Table 2).

The research shows that annual weeds were dominant in the spring barley (Table 2) and accounted for 88.3% of all weeds in the crops. Annual monocotyledonous weeds were the most prevalent in all parts of the hill out of annual weeds, accounting for around 72% of all weeds. *Echinochloa crus-galli* L. and *Poa annua* L. made up the biggest part of weeds that were dominant in the spring barley ripening stage.

The quantity of weeds and their dry matter mass differences largely depend on the composition of weeds in barley agrophytocenosis, or the ratio between annual and perennial weeds [18].

## Weed DM mass in the spring barley crop

It has to be noted that the dry matter mass is a more dynamic indicator of weediness in the agrophytocenoses rather than the amount of weeds. This depends on the weeds, especially in perennial single plants in the uneven development agrophytocenoses, because together with the higher developmental stage the weed mass is increasing) [18].

Analogous results were found while analyzing weed dry material mass (DM) data in spring barley (Table 2). The biggest amount (85%) of total weed DM mass on all parts of the hill was made up of annual weeds; 70% were annual monocotyledonous weeds (Table 4). *Poa annua* L. and *Echinochloa crus-galli* L. (respectively 0.64–45.49 and 8.25–92.39 g m<sup>-2</sup>) had the biggest DM mass out of the latter plant group. *Poa annua* L. was progressively increasing from the hill summit to the footslope, while the *Echinochloa crus-galli* L. was decreasing in numbers from the hill summit to the footslope. The largest DM mass of annual dicotyledonous was determined on the midslope of the hill, on average 25.11 g m<sup>-2</sup> and that is 2.4 times more than on the summit of the hill and 3.2 times more than on the footslope (Table 4). *Viola arvensis* Murr. were found to have the largest mass out of all annual weeds on the midslope of the hill (19.6 g m<sup>-2</sup>).

The largest DM mass out of all perennial weeds was that of *Agropyron repens* L. (0.51–9.22 g m<sup>-2</sup>), located on the footslope of the hill, and it is mostly prevalent during the ripening stage of spring barley. *Equisetum arvense* L. DM mass was determined to be from 2.29 to 21.23 g m<sup>-2</sup>.

The weed DM mass on the summit of the hill was 1.5 times bigger than on the midslope and 1.6 times bigger than on the footslope (Table 4). The correlation of research results showed that during the heading ( $r = 0.886^{**}$ ) and ripening ( $r = 0.886^{**}$ ) stages the weed mass (x) and weed number (y) were highly correlated. Weed DM mass was also reliant on spring barley density. There was a strong correlation between weed DM mass and spring barley total and productive stem amount, respectively  $r = 0.671^*$  and  $r = 0.707^*$ .

## Spring Barley crop soil seed bank

Seeds enter the soil through many sources, but the major source is plants that escape control and produce seeds within the field [19] found that weed seed bank response to differing weed control practices during a 4-yr experiment depended on the initial weed density [20]. Weed seed bank analysis provides knowledge on the effect of agricultural management practices on weed community dynamics [21].

The lowest amount (4764 seeds m<sup>-2</sup>) of viable weed seed bank in the constant seed bank of the soil was in the summit of the hill compared to the midslope and the footslope (Figure 1 and 2) in the beginning of plant growing season on a hilly relief. There were respectively 2.5 and 2.2 times more weed seeds found on the midslope and the footslope of the hill's soil. A similar weed seed amount was discovered in the depths of 0–5 and 5–15 cm of the soil on all parts of the hill. Out of the total weed seed amount, 53.4% were discovered on the summit in the soil depth of 0–5 cm, 50,9% – on the midslope, and 55.0% on the footslope (Figure 1). *Chenopodium album* L., *Viola arvensis* Murr. and *Fallopia convolvulus* L., accounted for the biggest amount of seeds on all parts of the hill.

It was discovered that during the end of growing season, there are 3.8 times more weed seeds in the spring barley crop soil compared to the beginning of growing season (Figures 1 and 2). There were 75.6-79.00 % of weed seeds in the soil depth of 0-5 cm. The soil on the

summit was discovered to be the most (43377 seed m<sup>-2</sup>) contaminated with weed seeds (Figure 2). The seeds of *Setaria viridis* P. B., *Chenopodium album* L. and *Viola arvensis* Murr. were the most common on the summit of the hill, the seeds of *Erysinum cheiranthoides* L., *Setaria viridis* P. B., *Veronica arvensis* L. and *Spergula arvensis* L. – on the midslope, while the seeds of *Viola arvensis* Murr., *Erysinum cheiranthoides* L. and *Veronica arvensis* L. – on the footslope of the hill.

Literature states that the majority of seeds entering the seed bank come from annual weeds growing in the fields. The size of the seed bank reflects past and present field management [22].



Fig. 1. Weed seeds number in the spring barley crop soil in the beginning of growing season. Kaltinėnai, 2020 m.







# CONCLUSIONS

When comparing the impact of different parts of the hill it can be essentially concluded that a bigger permanent weed number is determined during the heading and ripening stages of spring barley on the summit of the hill.

Substantive differences were determined in the perennial weed group during the heading stage of spring barley. Essentially less of the latter weeds were determined on the midslope or the footslope. During the later growing season period, when the *Echinochloa crus-galli* L. was distributed and the barley was in the ripening stage, significant differences were determined in the annual weed group. The spreading of *Fallopia convolvulus* L. did not depend on the relief conditions.

In the conditions of a hilly relief, during the beginning of growing season, the lowest amount of viable weed seeds in the constant soil seed bank was determined on the summit of the hill. During the end of the growing season there are 3.8 times more weed seeds in the spring barley crop soil compared to the beginning of growing season. The seeds of *Setaria viridis* P. B., *Chenopodium album* L., *Viola arvensis* Murr., *Fallopia convolvulus* L., and *Erysinum cheiranthoides* L. accounted for the biggest amount of all weed seeds in all parts of the hill.

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# THE PRIMARY SEASON OF APPLE SCAB UNDER CHANGING CLIMATE CONDITIONS

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#### ABSTRACT

Apple orchards protection against the apple scab (*Venturia inaequalis* (Cooke) Wint.) is one of the most important problems in the apple growing. Guidelines for integrated fruit production prescribe use of forecasting systems in a plant protection for a correctly timing of primary season fungicide sprays. In Latvia decision support system for managing apple scab, RIMpro (RIMpro B.V., Zoelmond, Netherlands) has been used for several years. RIMpro incorporate a model basically comprised of two components, an ascospore maturity model and an infection period model, it accounts for spore death due to leaf litter decomposition and leaf wetness duration inadequate to promote infection.

The apple scab fungus overwinters in fallen leafs. Late winter development of the fungus is insufficiently understood to allow the date of first mature ascospores to be calculated. Therefore RIMpro uses the first observed ejectable ascospores as start date – biofix to start the simulations. RIMpro has four options for setting the biofix, in a preferential order: 1) first ascospores discharged in the lab via Petri-plate assay; 2) first spores observed in the field using spore traps; 3) first mature spores observed in squash mount or 4) green-tip stage of main scab susceptible cultivar on site. The model provides the most accurate outputs if the biofix for spore release based on the actual testing is entered in the system. This biofix is usually determined by using a spore trap and requires special equipment and expertise therefore in the most cases, the date of green tip alone for the spore release biofix is used if data on first spore release is not available. Observations from several researchers shows, that in Europe, in the past 30 years, the average date of apple green tip has become 12 days earlier, and the average date of first ascospore ejection is now 24 days earlier than in 1985.

Also in Latvia the green tip stage is most often used as biofix to start forecasting of the apple scab. From 2012 to 2020 seven site-year combinations were observed and various data collected to determine whether there are changes in the primary season of the apple scab in Latvia. The earliest green tip stage was recorded on 28 March in 2020 in the southwest part of Latvia, the latest – on 5 May in 2013 in the northeast and the northwest part of Latvia. The time of the green tip stage was variable over the years and it was mainly dependent on temperature. The primary season in 2013 generally started later in early May on all orchards, while in 2020 it was the earliest beginning of vegetation at the end of March. A period of nine years is too short to assess whether climate change has had a significant impact on the onset of apple orchard vegetation. However, it has been observed that more often a few ascospores are ejected weeks before green tip, indicating a shift towards earlier maturation. In the meantime, long dry periods during the first months of ascospore maturation and discharge slow down the maturation, leading to ascospore ejection later in season than expected. Despite the early date of biofix, the first significant risk of infection forecasted by RIMpro was often reached only in the end of April or in May. This means that it would be necessary to determine the actual start of spore ejection in order to make the forecast as accurate as possible in order to avoid unnecessary fungicide applications.

Keywords: RIMpro, incidence level, green tip stage, apple cultivars, fungicide applications

# EFFECT OF BIOLOGICAL SEED TREATMENT PRODUCTS ON PLANT DEVELOPMENT AND CONTROL OF SEEDLING BLIGHT IN SPRING WHEAT

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#### ABSTRACT

Seed health, uniform and fast germination have positive effect on crop vigour not only at early growth stages, but during whole season as well. Seed-borne pathogens as *Fusarium spp.*, *Tilletia caries* and some other can be very destructive pathogens, causing significant yield losses, therefore their control can be very important. Chemical pre-sowing seed treatment is the main approach in control seed infections. Biological control is more environmental-friendly and can be considered as a tool in efficient pest management.

Aim of the study was to evaluate effect of biological products on seed germination and efficacy against seedling blight at early growth stages of spring wheat. Experiments in controlled and natural field conditions were carried out in the spring of 2020. Two biological products, Biomas Protect (*Bacillus amyloliquefaciens*) and Biomas Universal (*Bacillus subtilis*) were used to treat seeds separately and in a tank mix with commercial chemical seed treatment fungicide (STF) Celest Trio (25 g/l fludioxonil, 25 g/l difenoconazole, 10 g/l tebuconazole) at rate 1.5 l t<sup>-1</sup>. Seed germination, seedling development, severity and incidence of seedling blight were evaluated in field and laboratory experiments.

The results of these experiments suggested that, in comparison with control, germination of treated seeds was slightly lower regardless of used product. Although, biological products used together with chemical seed treatment fungicide had slightly lower reduction of seed germination compared to STF alone. Biological products slightly improved seedling and root growth. This increase observed compared both to STF and to seedling from untreated seeds. Data of experiments suggested that the best control of seedling blight was established in plots where tested products were used together with chemical seed treatment fungicide.

Keywords: seed treatment, biological products, seedling blight, spring wheat

# **INTRODUCTION**

Cereals are widely grown in Lithuania and takes more than half of all crops in agriculture. Most of all harvested area of agriculture crops consists of winter wheat, and according to official data, spring wheat was second most cultivated crop in Lithuania up until 2018. As the population and demand for food continue to grow it is important to ensure healthy and productive crops from early growth stages.

Seed-borne pathogens such as *Tilletia* spp. and *Fusarium* spp. are causal agents of various wheat diseases and uncontrolled can cause considerable impact on quantity and quality of yield [1]. It is well documented that fungi of genera *Fusarium* are causing agent of seedling blight, crown rot and root rot in wheat [2]. In addition, infection of *Fusarium* species on grain also is a major concern as it may result in lower seed germination, plant vigour and growth and development of juvenile plants or seedlings [3, 4].

Pre-sowing seed treatment is efficient way to control seed- and soil-born fungi, usually by applying chemicals substances on seed [5]. However, there is a growing body of literature that recognises the importance of integrated pest management (IPM) – a sustainable strategy for managing pests regarding both economical and environmental aspects of agriculture. The

concept of IPM considers all possible methods for crop protection, including usage of more environmental-friendly biological products [6].

The existing body of research on microbial biocontrol suggests that bioproducts could be seen as a possible alternative to synthetic fungicides [7]. Biocontrol agents include antagonistic active microscopic fungi and bacteria. Previous research notes that of bacteria, genera *Bacillus*, are one of the most studied biological control agents in scientific literature [8]. Strains of *Bacillus subtillis* [9] and *Bacillus amyloliquefaciens* [10] are recognised as effective measure against root and stem base diseases in cereals, although more research is necessary to promote biological products as disease control agents in integrated pest management strategies [11]. Furthermore, some researchers indicate that biological agents, such as *Bacillus subtillis*, are compatible with lower rates of fungicides and might be used together for better disease management [12].

The objectives of the study were: (i) to evaluate effect of seed treatment with bioproducts on seed germination and vigour; (ii) to evaluate efficacy of seed treatment with bioproducts, based of *Bacillus subtillis* and *Bacillus amyloliquefaciens*, against seedling blight in spring wheat; (iii) to evaluate the effect of bioproducts used together with chemical seed treatment fungicide (STF) on seedling blight, seed germination and vigour.

# MATERIAL AND METHODS

#### Seed treatment

The study was conducted in 2020 at the Department of Plant Pathology and Protection of Institute of Agriculture, Lithuanian Research Centre for Agriculture and Forestry. Spring wheat cv. 'Flippen' were treated by using liquid seed treatment equipment 'Hege 11' according to the scheme below (Table 1). Treated seeds were used in both field and controlled environment experiments.

Trt. No.	Treatment	Active ingredients	Dose l ha <sup>-1</sup>
1.	Untreated	_	—
2.	Biomas protect	Bacillus amyloliquefaciens	0.1
3.	Biomas universal	Bacillus subtillis	0.1
4.	Celest Trio	25 g/l fludioxonil, 25 g/l difenoconazole, 10 g/l tebuconazole	1.5
5.	Biomas protect + Celest Trio	25 g/l fludioxonil, 25 g/l difenoconazole, 10 g/l tebuconazole	0.1+1.5
6.	Biomas universal + Celest Trio	25 g/l fludioxonil, 25 g/l difenoconazole, 10 g/l tebuconazole	0.1+1.5

Table 1. Seed treatment scheme

## Field experiment and design

Spring wheat for field experiment was sown with a small plot drilling machine 'Wintersteiger Kubota' at seed rate of 550 viable seeds per square meter. The experimental plots were 1.5 m in width and 10 m in length. All plots were arranged in randomized blocks in four replicates. Common plant growing practices were used in the experiment.

## Seed germination and seedling tests

To evaluate seedling growth and primary infection *between-paper method* was used [13]. 50 seeds were placed in a line in 2 cm distance on wet 20 cm x 100 cm filter paper. Seed then covered with another 7–8 cm moist filter paper strip and 15 cm width parchment paper and loosely rolled. For every experimental treatment totally 200 seeds were used. The rolls then were placed in separate glasses with distilled water (water level lower than 5 cm to seed) and incubated in room temperature for 21 days.

After 3 weeks rolls were carefully rolled out and germinated and not germinated seeds counted. Furthermore, in accordance with typical colour and shape of fungi colony, genera of fungi were visually identified in each roll. Healthy and damaged seedlings were counted to assess the severity and incidence of the disease. Severity of symptoms on seedling base and root were evaluated by 0-3 scale: 0 – healthy, 1 –slightly damaged and affected area is <50 %, 2 – symptomatic area of tissue >50 %, 3 – all damaged or seedling is dead [14].

Plant development and vigour was evaluated by seedling height and root length measurements.

For test of germination energy and viability germination test according to International Seed Testing Association (ISTA) approved methods. 100-seed samples in four replicates were collected and germinated in Petri dishes on moist filter paper. Dishes were incubated in controlled environment at 20°C temperature. Seed germination energy and vigour were evaluated after 4 days and germination after 7 days [15].

# Field germination and assessments

Field germination was evaluated by counting number of emerged seedlings on five 2-m length rows diagonally across the plot. Counting was conducted twice: first at the beginning of emergence (50% of plants emerged in control plots) and second at when plants fully emerged (two-leaf growth stage (BBCH 12)).

Infection level of seedling blight in field experiment was assessed at the beginning of tillering (BBCH 21) by 30 randomly picked seedlings from each plot. Plant damage was evaluated by 0-3 scale. Severity of symptoms on seedling base were evaluated by 0-3 scale: 0 – healthy, 1 –slightly damaged and affected area is <50 %, 2 – symptomatic area of tissue >50 %, 3 – all damaged or seedling is dead [14].

# Methods of statistical data analysis

*Statistical analysis.* The analysis of data was made with software package SELEKCIJA using the analysis of variance method (ANOVA). To determine the differences between treatments Duncan's multiple range test was used (P < 0.05) [16]

# RESULTS

# **Effect on germination**

Effect on germination of biological products and their combination with chemical seed treatment fungicide (STF) on spring wheat was evaluated in controlled environment and in field experiment (Table 2). In controlled environment, seeds treated with biological products alone showed similar germination and germination energy as untreated seeds. In contrast to that, tank mix with chemical STF and biological products had negative effect on germination and seed energy compared both to untreated seeds ant to seed treatments with biological products used

alone. Although, other researchers found that chemical seed treatment fungicides greatly enhance seed germination [17]. The results of this study on contrary indicate that chemical seed treatment had negative effect to seed germination both in field and controlled environment experiments compared to untreated control. Our data might coincide with results obtained by Hysing and Wiik [18], where chemical STF had no effect on spring wheat density. Data of field experiment suggested that bioproducts used alone and together with chemical STF performed similar and no significant differences were recorded.

No.	Treatment	Germination energy in lab, %	Germination in lab, %	Germination in field, %
1.	Control	97,25 c	97,50 cd	82,29 b
2.	Biomass Protect (0.1 1 t <sup>-1</sup> )	94,75 bc	94,75 bcd	75,00 ab
3.	Biomass Universal (0.11t <sup>-1</sup> )	96,50 bc	97,75 d	77,89 ab
4.	Celest Trio (1.5 l t <sup>-1</sup> )	84,50 a	93,50 b	72,40 ab
5.	Biomass Protect $(0.1 \ l \ t^{-1})$ + Celest Trio $(1.5 \ l \ t^{-1})$	85,00 a	93,25 ab	78,45 ab
6.	Biomass Universal $(0.1 \text{ l/t})$ + Celest Trio $(1.5 \text{ l/t})$	84,00 a	90,00 a	77,62 ab

Table 2. Effect of biological seed treatment products on seed germination (%)

Means followed by same letter do not significantly differ (P<0.05, Duncan's Multiple Range Test).

# Effect on seedling development

Resent research has established that certain strains of *Bacillus subtillis* can affect production of phytohormones, thus increasing the growth of plants [19]. The evaluation of different seed treatments effect on plant development and vigour, expressed as seedling height and root length, was made. (Table 3). Assessed data from controlled environment suggests that bioproducts affected plant development positively. *Bacillus amyloliquefaciens* based Biomass Protect and *B. subtillis* based Biomass Universal used as solo products for seed treatment had increasing effect on seedling height and on root length compared to untreated control. The addition of Biomass Protect to chemical STF resulted in lower reduction of seedling growth by 4% and root length increase by 11 %. However, biological products used in tank mix with chemical STF, showed no significant effect on seedling development compared to chemical treatment only.

No.	Treatment	Seedling height, cm	Root length, cm
1.	Control	22,5 b	19,2 abc
2.	Biomass Protect (0.1 l t <sup>-1</sup> )	23,7 bcd	21,0 abc
3.	Biomass Universal (0.1 l t <sup>-1</sup> )	24,9 d	22,4 c
4.	Celest trio $(1.5 \mathrm{l}\mathrm{t}^{-1})$	16,3 a	19,6 abc
5.	Biomass Protect $(0.1 \text{ l t}^{-1})$ + Celest trio $(1.5 \text{ l t}^{-1})$	17,0 a	21,9 abc
6.	Biomass Universal $(0.1 \text{ l/t})$ + Celest trio $(1.5 \text{ l t}^{-1})$	15,7 a	19,1 a

Table 3. Effect of biological seed treatment products on seedling development (cm)

Means followed by same letter do not significantly differ (P<0.01, Duncan's Multiple Range Test).

# Efficacy against seedling blight and root rot

In controlled environment grown seedlings were examined in order to evaluate seedling stem base and root damage by seed-borne pathogens (Fig. 1 and Fig. 2). From data presented in Fig. 1, it is obvious that Biomass Universal (*B. subtillis*) mixed with STF had slightly higher efficacy against seedling blight; other than that, no clear control of the disease was recorded. Efficacy of Biomass Universal did not differ from chemical STF.



Fig. 1. Efficacy of seed treatments against seedlings blight in controlled environment, %. Means followed by same letter do not significantly differ (P<0.01, Duncan's Multiple Range Test)

Furthermore, from the data presented in Fig. 2, we can see that there is a clear difference of efficacy between seed treatments on root damage. All used products lowered disease severity on roots. Biological product Biomas Protect (*B. amyloliquefaciens*) showed only a slight effect against the disease; in contrast to that, seed treatment with Biomas Universal (*B. subtillis*) established significant efficacy against root damage by pathogens compared to untreated control. The results of our experiment suggested that chemical STF combined with biological products was more effective against root pathogens. These results reflect those of W. Sameer [12] who found that *B. subtillis* used together with fungicides tend to have better control of root root in wheat.



Fig. 2. Efficacy of seed treatments against root damage in controlled environment, % Means followed by same letter do not significantly differ (P<0.01, Duncan's Multiple Range Test)

In the field trial the severity of seedling blight in untreated plots was 34.2 %. Fig. 3 presents data obtained from field trial assessment showing efficacy of different seed treatments against root damage in spring wheat. The results indicate that all tested seed treatments had control of plant base disease. However, obtained results were insignificant. Only B. Protect (*Bacillus amyloliquefaciens*) mixed with chemical STF established statistically reliable efficacy against the disease compared to untreated control. In this field experiment, no significance regarding seedling blight control recorded between treatments.



Fig. 3. Efficacy of seed treatments against root damage in field, % Means followed by same letter do not significantly differ (P<0.05, Duncan's Multiple Range Test)

Although existing research recognises seed treatment with fungicides as highly effective control method against diseases in early growth stages [18], efficiency of seed treatment can be

limited by other factors such as meteorological conditions, cultivation and crop rotation [20]. In this study efficacy of both biological and chemical seed treatments were low.

In summary, one-year results of this study imply that biological seed treatment had no positive effect on seed germination and germination energy, however slightly positive effect on seedling development was recorded. Moreover, biological products reduced negative effect of chemical STF on seed germination and seedling development when used together. *B. amyloliquefaciens* and *B. subtillis* based products had slight decreasing effect on seedling blight severity. In addition, biological seed treatments used together with chemical STF enhanced the efficacy against root and stem base diseases. Based on our research we could suggest that *Bacillus* strains could be potentially used together with chemical STF for better plant development and higher efficacy against seedling blight. However, the different rate proportions of biological products and chemical STF could be further investigated.

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# DETERMINING THE EFFECTIVE PERIOD OF FUNGICIDES AGAINST ZYMOSEPTORIA TRITICI

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#### ABSTRACT

*Zymoseptoria tritici* is the causal agent of Septoria tritici blotch (STB) in wheat and its spread is reported to depend on environmental conditions. The primary source of inoculum is sexual ascospores, which are dispersing from previous wheat stubbles and infecting young plants in autumn. In spring the pathogen forms the asexual spores (conidia), which rain splash moves up the plant causing secondary inoculation. Disease spread is usually controlled by using fungicides, therefore selecting timings of application is crucial.

The study's objective was to estimate the effect of fungicide programs on STB severity and grain yield in winter wheat and to observe pathogen spore release during wheat growing seasons.

Two field experiments (in monoculture field and in field after non-host crops) were designed in winter wheat and six application programs were chosen. Fungicide Adexar (fluxapyroxad 62,5g  $1^{-1}$  + epoxiconazole 62,5g  $1^{-1}$ ) in dosages 1.0 and 2.01 ha<sup>-1</sup> was used for the disease control. For spore release evaluation Burkard spore traps were placed in monoculture and after non-host (2019 – peas; 2020 – winter oilseed rape). Both experiments and spore release observations were done from 2018 autumn till the middle of summer 2020.

In 2019, due to unfavourable meteorological conditions, plant infestation with pathogen was low. Nevertheless, in comparison of both rotations there were marked trends of higher severity of STB in winter wheat monoculture. In both experiments all tested programs resulted in a significant reduction of disease severity. However, the effect of fungicides on yield was inconsistent. The difference between tested applications programmes was more precise at higher disease pressure in 2020. In a comparison of fungicide application programs in both experiments the most efficient application timing was when two applications were done (T1 (first application) 8-10 days after rain; T2 (second application) 2 weeks after T1). This program significantly reduced STB severity and significant yield increase was established, compared to other tested programs.

The evaluation of spore release results showed that two spore spread peaks were determined. One in autumn – from the beginning of October and another in late spring – May. Between two different crop rotations more intensive spread of ascospores in monoculture was in spring-summer periods; meanwhile, in winter wheat grown after non-host – in autumn.

Overall, the results of this study indicate that the most effective control period against STB is when fungicide application times are chosen based on weather conditions.

**Keywords:** application programs, AUDPC, septoria tritici blotch, winter wheat, *Zymoseptoria tritici*, ascospores

# EFFECTS OF INSECT MASS OUTBREAKS ON SCOTS PINE FOREST ECOSYSTEM FUNCTIONING AND SOIL HEALTH IN THE PROCESS OF CLIMATE CHANGE

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#### ABSTRACT

Forests are pivotal and vital for people, since they characterize a huge importance of ecology and economy factors all around the world. Scots pine (Pinus sylvestris L.) is one of the conifers species with a wild range distribution, and it is the most common species in Lithuania, where forests are the primary resource for its economy. Moreover, Scots pine is very important for the ecological aspect, owing to its ability to grow in poor sands soil where other species cannot germinate. Nowadays, in the process of climate change, there are more insect mass outbreaks on Scots pine forests than has ever been; therefore, science research and consciousness of strategy systems for protection against insect mass outbreaks and analyses of forest biodiversity changes during the outbreaks are a breakthrough process in forestry. Insects and microorganisms are some of the most evolutionary variable organisms characterized as deep species and mutual relationships diversity with unique qualities of adaptation in the forest ecosystem. One of the hazardous insect mass outbreaks for Scots pine forests in Lithuania has proceeded by nun moth (Lymantria monacha L.), which repeats every 10-15 years. The last outbreaks were fixed in 2018 and have repeated every summer since then. For protection, it has been used biological spray made by Bacilus thuringiensis bacterium. Even though the spray is eco-friendly, there are a lot of obscurities inhow it affects fungi of stands phyllosphere and soil. Analyses of Lymantria monacha outbreaks and prevention tools exposure for forest fungi diversity, soil health, and vitality of other insects are crucial in creating sustainable Scots pine stands and determining black arches expansion principles in the future.

Keywords: pests, Pinus sylvestris, microorganisms, tree diseases, Lymantria monacha

#### **EXTENDED ABSTRACT**

Insect pests are one of the main forest ecosystems biotic components that cause tree disturbances on a high scale. The pests play an important role in forest ecosystems when they are controlled and do not form outbreaks [1]. However, anthropogenic activity, incidental exotic pest species introduction, forest fires, tree diseases and unfavourable weather can weaken the trees, open a room for insect outbreaks and cause intense forest ecosystems derangements [1], [2]. The pest outbreaks have an indirect negative impact on people and forest animals through the trees that are a pivotal and vital factor in our lives and in our nature, especially in the process of climate change [3]. Analyzing exposure of climate change on insect pest life stages, biodiversity of microorganisms and pests-microorganisms relationship is highly important to create tools and models that could increase prediction of the pests speed and their spread in the future [4].

*Pinus sylvestris* is one of the tree species distinguished a wild range distribution in temperate and boreal zones in Europe, Asia and North America continents [5], [6]. Moreover, Scots pine characterizes unquestionable benefit in Lithuanian forests, where occupies 1/3 of all forested areas [7]. The tree is very important owing to its ability to grow in poor sands soil where other tree species cannot germinate [8]. Furthermore, Scots pine has infinitely large therapeutic properties for people's health. First of all, the environment of Scots pine stands enhances human intracellular anti-cancer proteins, natural killer cell activity and natural killer cells quantity [9].

Secondly, Scots pine emits many phytoncides that help relieve stress, uneasiness, enhance immune system function, and quality of sleep [10]. Finally, the species is essential as a source of timber production [11]. To sum up, Scots pine is a tree species necessary to maintain and analyze principles that would help to preserve this kind of tree as healthy as possible.

Scots pine is a species of tree that does not have a large variety of insect pests compared to other forest tree species. However, some forest-defoliating insects reach outbreaks levels and have a hazardous effect, causing tree defoliation [12]. The trees can withstand the outbreaks, but when they repeat a few summers constantly, they cause tree mortalities [13]. Scots pine defoliators are highly related to climate, and their biodiversity is bigger in drought areas. It follows the relationship between pests range and a sea level.

Moreover, the biodiversity of forest defoliators depends on the stands particular ages [14]. One of the most recurrent and dangerous pests on Scots pine in Central Europe is *Lymantria monacha* insect, which grubs gnaw the tree needles in the early summer [15]. Unfortunately, the pests replace the functioning of Scots pine ecosystems, which are not well-known in the process of mass outbreaks. Researchers perform analyses with the purpose to determine insect mass outbreaks influence on stands functioning, which is highly related to the mutual interaction of forest microorganisms [16].

Lymantria monacha mass outbreaks repeat every decade in Eastern Europe, and warmer climatic conditions stimulate the pest spreading to colder regions in northern Europe [15], [17]. During the last 20 years, the pest has expanded to Eastern Finland by 200 km, and it has been expanding continuously. Based on Finland scientists, the northward expansion rate of Lymantria monacha was up to 17.1 km every year from 2007 to 2013, and the expansion rate was bigger than 2000-2006 years [15]. To understand warmer climatic conditions' impact on Lymantria monacha outbreaks formation, we have to analyze the pest life stages and their relationship with forest microorganisms. Adult of the insect fly from the middle of summer to the beginning of September, and each female lays down up to 300 eggs in Scots pine bark crevices. The embryo of the insect ends its development after 1-2 months, approximately, and then comes a pause for 2 and a half month and during this time the embryos are scatter by wind alongside [18]. In this time, there are significant cold winters that break the pest embryos ant they become dead [15]. The pest expansion highly related to winter cold, and if the winters are warmer than usual, Lymantria monacha embryos stay alive, and the beginning of the outbreaks starts in May when the pest grubs are prepared to gnaw Scots pine needles [18]. Usually, the mass outbreaks repeat 2 or 3 summers in a row, depending on protection agents used in the process of insect pest mass outbreaks. There are chemical, biological control ways to protect Scots pine forests from Lymantria monacha. However, when the outbreaks are fixed. The primary agent is using a biological product ("Foray 76B") made from the bacteria Bacillus thuringiensis [19]. The spray's activity is positive evaluated for the destruction of the pest grubs, and it does not harm pest adult, natural enemies of the pest and other animals [20]. Despite the positive effect, the action of biological product from Bacillus thuringiensis has not explored in soil, where an abundance of microorganisms forms harmonious ecosystem functioning. It is important to analyse how Lymantria monacha mass outbreaks and protection agents change the biodiversity of microorganisms to improve protection mechanisms, predict future insect mass outbreaks, and create schemes with as small as possible harm for all Scots pine forest ecosystem functioning [21].

Insect pests characterize high reproduction and mobility rates that let them instantaneously adjust to environmental conditions that regularly change, especially in t climate change [12]. Natural pest killers have slower reproduction and mobility rates than insects, and it is one of the reasons why the mass outbreaks can regularly comprise every decade [17]. The insect mass outbreaks significantly alter ecosystem functioning in forests, which is highly related to microorganism biodiversity during the mass outbreak process. Soil microorganisms are

important in good quality forest ecosystems through the cycling of nitrogen which is an essential nutrient for ecosystem organisms [16]. These microorganisms constitute a majority part of the biodiversity in soils and are vital for forest ecosystems [22].

On the other hand, forest microorganisms and pest insects can act each other and make a symbiotic relationship [23]. When symbiosis between insects and microorganisms is native, trees do not weaken and ecosystem works well for the trees health. However, if insect pests or microorganisms are exotic, their symbiosis can damage the trees and cause tree deaths [24]. All in all, due to soil microorganisms importance of nitrogen cycling and also insect pests and microorganisms attribute to make symbiosis, it is very important to establish variety, alteration of microorganisms and their interaction with the insect during the process of insect pests mass outbreaks and it would help to maintain healthier forests in the future [16], [24]. In our analysis, we collaborate with the Institute of Forestry, Lithuanian Research Centre for Agriculture and Forestry scientists. We are working on establishing Scots pine phyllosphere and soil microorganism diversity and soil health in the process of *Lymantria monacha* mass outbreaks. This research would be a benefit in a way to predict the mass outbreaks formation tendencies in the future and to create better maintenance strategies that help us to preserve Scots pine forests biodiversity.

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# **CONFERENCE PAPERS**

1

# III.4. Food sciences and technologies

I. Pauliukaitytė et al. ELECTROSPUN POLYANILINE AND POLYETHYLENE OXIDE
FIBROUS CHEMOSENSOR FOR DETECTION OF GASEOUS BIOGENIC AMINES IN
PERISHABLE RAW MEAT PRODUCTS
V. Puzeryte et al. VARIATION IN PHENOLIC COMPOUNDS CONTENT AND
ANTIOXIDANT ACTIVITY OF DIFFERENT PLANT PARTS OF ARALIA CORDATA
(ARALIA CORDATA THUNB.)
S. Sidiropoulos et al. ENRICHED PLA FILMS WITH ANTIMICROBIAL FACTORS FOR
COATINGS AND FOOD PACKAGING
P. Štreimikytė et al. OPTIMIZATION OF COMMON BUCKWHEAT (FAGOPYRUM
ESCULENTUM M.) MULTIENZYME-ASSISTED WATER EXTRACTION AND
DETERMINATION OF HYDROPHILICITY
V. Adaškevičiūtė et al. OPTIMIZATION OF CONDITIONS FOR BEE POLLEN LACTIC
ACID FERMENTATION

# ELECTROSPUN POLYANILINE AND POLYETHYLENE OXIDE FIBROUS CHEMOSENSOR FOR DETECTION OF GASEOUS BIOGENIC AMINES IN PERISHABLE RAW MEAT PRODUCTS

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#### ABSTRACT

The formation of biogenic amines in the perishable raw meat products are one of the first signs of food spoilage. This may happen because of improper product storage conditions, microbiological contamination during the packaging, or simply due to the natural maturation. Biogenic amines not only reduce the organoleptic properties of products but also are harmful to human health because of their toxicity. The quality of meat may be assessed using sophisticated techniques, but faster and cheaper ways to detect spoiled food products are important for the efficient shelf-life control.

We have developed a Polyaniline and Polyethylene oxide fibrous sensor, which is sensitive to biogenic amines (such as Cadaverine, Spermine, Putrescine, Spermidine) resulting from the decarboxylation of specific free amino acids. In the polyaniline-polyethylene oxide sensor matrix, polyaniline works as a sensing material and reacts with Cadaverine, resulting in a color changing reaction visible to the naked eye. The sensor matrix has been developed using electrospinning technique. The experimental variables related to materials (types of polymers and their concentration, as well as solvent ratio) and electrical process (tip-to-collector distance and voltage, as well as duration of spinning to achieve stable and solid sensor that could be applied and tested on food) were researched. The obtained matrix has been characterized for its morphology (Scanning Electron Microscopy analysis) and reactivity to pure Cadaverine vapour.

The simplicity of the Polyaniline-Cadaverine reaction is a key of a cheaper and faster way to detect formation of biogenic amines and prevent possible poisoning with the spoiled meat products, by installing directly in the packaging of the meat products.

Keywords: biogenic amines, polyaniline, sensor, nanofibres, electrospinning

## **INTRODUCTION**

In the past few decades, an increasing focus on ensuring food quality and safety has been noticed. Scientists are looking for fast, simple, reliable, and low resources required methods to detect the beginning of food deterioration. The detection of early stages of food deterioration could prevent food poisoning and health problems [1].

After estimating the meat consumption on a global scale, high resources that are required for the growth of raw material of meat products and rapid spoilage it is important to detect and prevent perishability of these products in time [2]. The most common meat spoilage microorganisms are *Pseudomonas*, lactic acid bacteria (LAB), *Enterobacteria* and *Bronchlothrix thermosphacta*. Deterioration process of meat products is often caused by a low concentration of oxygen, inappropriate temperature conditions, optimal water availability and unsterile equipment in slaughterhouses. These conditions are ideal for microbial growth [3].

During the process of meat products deterioration, the formation of biogenic amines (BA) has been noticed. These substances are potentially toxic and excessive oral intake can cause headaches, stomach aches, nausea, and other serious health problems. Biogenic amines are produced during the decarboxylation of amino acids caused by microbiological contamination

[4]. Therefore, early detection of biogenic amines could notify about the contamination of particular meat products.

For the reason mentioned above colorimetric indicator that is sensitive to biogenic amines is a necessity. During the research polyaniline protonated form – emeraldine salt was used to detect principle BA – cadaverine [5]. The indicator was formed from fibres using the process of electrospinning. This technique has a growing interest and various application spheres due to its simplicity, inexpensive setup, large surface-area-to-volume ratio, optimal fibre diameters [6].

# METHODS AND MATERIALS

# Materials

- Polyaniline emeraldine salt (PANI ES)
- Polyethylene oxide (PEO)
- Camphorsulfonic acid
- Chloroform
- Sodium hydroxide (99%)
- Cadaverine (95%)

All the materials were purchased from Sigma-Aldrich.

# Methods

The homogeneous solution of the PANI polymer was obtained by dissolving PANI ES in camphorsulfonic acid and chloroform via mechanical stirring at room temperature. When PANI has completely dissolved the second polymer – PEO is added. The mixture of two polymers also stirred mechanically at room temperature till the homogeneity.

# Preparation of polymeric indicator

The electrospinning method was used to form PANI ES/PEO indicator. The prototype of the electrospinning apparatus was used for PANI ES/PEO fibres formation (Fig. 1). It consisted of a high voltage DC power supply, vertically positioned collector, one metallic needle and syringe pump. The grounded electrode in this system was a cylindrical collector another high voltage electrode was attached to the needle. Polymers solution was added to the syringe and fed through the horizontally fixed needle. The process of electrospinning was carried out at ambient conditions with the temperature around 23°C and humidity around 45% in an enclosed Plexiglas chamber. Other parameters of the PANI/PEO electrospinning were as follows: voltage 25 kV, feed rate 4 ml/h, tip-to-collector distance 17 cm, substrate – parchment paper.



Fig. 1. Scheme of the used electrospinning system [6]

### Test of indicator's sensitivity to a biogenic amine-cadaverine

During the experiment protonated polyaniline emeraldine salt was converted to its deprotonated form emeraldine base. This was reached by subjecting the PANI ES/PEO indicator to the gaseous form of the alkaline solution prepared from 282  $\mu$ l cadaverine and 200  $\mu$ l sodium hydroxide. The initial green color of the indicator changed to blue during the deprotonation reaction.

 $1 \times 2$  cm samples of parchment paper with electrospun PANI ES/PEO were attached at the bottom side of the 10 ml vial's cap. Cadaverine – sodium hydroxide solutions of the same concentration were added to the 9 identical 10 ml vials and left for 0 min, 5 min, 10 min, 20 min, 40 min, 80 min, 160 min, 320 min and 24 h. When the set time was over, the PANI ES/PEO samples were removed from the vials. There was no direct contact between PANI ES/PEO indicator and cadaverine – sodium hydroxide solution in the vial but deprotonation still has happened. The deprotonation reaction occurred because of the cadaverine nature feature to vaporize at room temperature.

The results were analysed using X-RiteColor spectrodensitometer and method of digital image colorimetry using Adobe Photoshop CS6 software package. To perform a method of digital image colorimetry, PANI ES/PEO indicators were photographed after the experiment with cadaverine. The further interpretations of the results are described in the results section.

# **RESULTS AND DISCUSSION**

#### Structural analysis of the electrospun indicator

The success of the electrospinning, fibres morphology and diameter were obtained from images of SEM analysis (Fig.2). Accurate results of diameter variations were obtained using ImageJ software package.


Fig. 2. SEM image of electrospun fibres of PANI ES/PEO indicator

Chosen electrospinning technique formed cylinder shaped fibres. The morphology of the obtained fibres mat is described as unsmooth, randomly orientated and porous. The smoothness and orientation are not the main keys that describe sensorial functions of the indicator but the porous matrix is an advantageous property. Because of the porosity of the sample, every surface area can be reached by the cadaverine gases faster and color response can be seen immediately.

Because of the proper choice of electrospinning parameters, fibres are not stuck together and orientated separately. The diameters of the fibre mat sample vary from 2,47  $\mu$ m to 5,84  $\mu$ m and the most common range appeared to be from 2,47  $\mu$ m to 3,47  $\mu$ m (Fig. 3).



Fig.3. Histogram of the fibres' diameters

In order to evaluate the statistical reliability of the obtained fibre diameters results, measurements of the mean and standard deviation have been made. The results were 3,92 µm and 1.04 accordingly. Graphically results are described in statistical chart (Fig. 4). The cross in the middle of the box stands for the mean result and the horizontal line represents the median. The most frequent results of the fibres diameters are in the middle of the box. The lowest value of the diameters is represented by the lowest horizontal line (below the box) and the highest value is marked with the highest horizontal line. No extreme or mild outfitters were detected.



Statistical analysis of fibres diameters

Fig. 4. Statistical distribution evaluation of the fibres diameters results

To prove that obtained statistical data are correct normal distribution (which is characterized by mean and standard deviation) was calculated. The results appeared to form a bell curve also known as Gaussian distribution. Gaussian curve proves that fibre diameters near the mean are more frequent than the far from the mean. In accordance with the box graph, the bell curve graphically illustrates the reliability of the obtained results of the fibre diameters.



Fig. 5. Bell curve of fibres diameters

# Sensory properties analysis of the electrospun indicator

Under the influence of biogenic amine cadaverine (in the gaseous state), electrospun PANI ES/PEO indicator changes its native color. Changes of the PANI ES/ PEO color in time are visible in Fig. 6.



Fig. 6. PANI ES/PEO indicator's reaction to gaseous cadaverine

The results of Fig. 5 illustrate the accurate deprotonation reaction of PANI ES/ PEO indicator. Exposed to cadaverine, the electrospun indicator changed its green color which is typical for the protonated form of polyaniline to the blue color, typical for the deprotonated color of polyaniline. The color changes were observed in time. Eye visible color changes appeared after 40 min of exposure.

# Spectrophotometric analysis with X-RiteColor spectrodensitometer

X-RiteColor spectrodensitometer allowed to evaluate the intensity of color elements. The obtained color differences after the experiment were converted into measurement data for descriptive color analysis. In this case, CMYK color model was analyzed and the accurate results were shown graphically in Fig 7.





Fig. 7 represents color changes in the CMYK spectrum of the samples in Fig. 6. In this model C (CYAN) and Y (YELLOW) values of the CMYK spectrum are the most important.

The Y value is high in the green sample and low in the blue sample. As the indicator's color is getting bluer over the time, the YELLOW curve is falling in the graph. The opposite dependence is with the C value. The bluer the sample gets the higher C value is expected. In Fig. 7 the CYAN curve is constantly rising because the sample exposed to biogenic amine over the time is getting bluer. B value in the CMYK model stands for Contrast [5]. In this model, B curve is also rising it shows that the indicator is getting darker (bluer).

# Digital image colorimetry using Adobe Photoshop software package

Digital image colorimetry is an innovative method to evaluate colorimetric changes of the sample. The method uses digital images of the samples captured with the digital camera [7]. The main advantages of choosing digital image colorimetry instead of traditional methods of analysis – speed, low-cost and simplicity [8].

In this PANI ES/ PEO indicator's (exposed to cadaverine) analysis Adobe Photoshop CS6 software package was used to evaluate the dominant color of Fig. 6 samples. Some scientists from previous scientific researches use RGB (RED, GREEN, BLUE) or CMYK (CYAN, MAGENTA, YELLOW, BLUE) color spectrum for digital image colorimetry [7]. But in this research the evaluation of green and blue color changes in the sample is the most relevant. Therefore, pixels of green and blue color types with corresponding tolerance were evaluated. Measurements of green and blue color pixels were compared with a total quantity of pixels in every sample. The results are presented in Fig. 8.



Fig. 8. Blue and green color ratio in the samples

Digital image colorimtery showed ongoing differences between blue and green color values. In Fig. 8 the green curve which represents green color is continously falling down. However, the blue curve (blue color) is steadily increasing. The dominance of blue color corresponds with the indicator's exposure to cadaverine over the time.

# CONCLUSIONS

The prototype of PANI ES/ PEO electrospun indicator reacting to a biogenic amine – cadaverine was generated and proved its high sensitivity and efficiency. The process of electrospinning appeared to be a useful method for the development of the indicator because of

the large surface area of the electrospun fibres mat. In this study SEM, spectrophotometric and Digital image colorimetry analysis was used.

Results from SEM analysis showed that diameters, morphology, porousness of electrospun PANI ES/ PEO fibres are optimal and appropriate for the indicators' structure and sensory parameters.

Obtained spectrophotometric results confirmed the indicator's sensitivity to biogenic amine and evaluated color changes in a quantitative method.

Digital image colorimetry measured the exact time when the blue color became dominant and the green color disappeared. In this study, the research showed that 240 min exposure to cadaverine solution is enough for blue color in the indicator to become absolutely dominant.

The importance and high potential of PANI ES/PEO indicator and the presented evaluation methods could be applied in the food industry and manufacturing areas.

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# VARIATION IN PHENOLIC COMPOUNDS CONTENT AND ANTIOXIDANT ACTIVITY OF DIFFERENT PLANT PARTS OF ARALIA CORDATA (ARALIA CORDATA THUNB.)

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#### ABSTRACT

There has been worldwide interest in plants with the same or similar bio stimulatory properties as ginseng (*Panax ginseng*) in recent decades. However, ginseng also has other botanical relatives (ginseng belongs to the genus *Aralia*). For a long time, no one even thought to try and replace the legendary ginseng. However, botanists, based on a careful comparative study of reproductive and other plant organs, have found a close relationship between ginseng and *A. cordata. Aralia cordata* is an essential medical herb belonging to the family *Araliaceae*, native to Asia. This plant has been acknowledged as a medical herb with anti-nociceptive, antidiabetic, antioxidant, and anti-inflammatory activities in China, Japan, and Korea [1]. This plant also grows in Lithuania but is not yet widely known and used. It is produced only by some Lithuanian herbalists and folk medicine specialists.

The root of *A. cordata* has been used as a traditional Chinese medicine for rheumatism and lameness [1]. It shows pharmacological activities, for instance, analgesia and hypothermia [2]. Diterpenes have been detected how analgesic and anti-inflammatory agents of this plant root [2, 3]. Additionally to diterpenes, this plant root contain valuable substances as polyacetylenes, saponins, lipid glycerol, and sterols [4, 5]. Also, phenolics compounds, nucleotides, saccharides, and alkaloids were found [6]. The previous studies reported that *A. cordata* roots could help regulate lipid metabolism and prevent lipid metabolism disorders and complications [7].

Most previous studies have focused on the root of *Aralia cordata*; however, the other part of the plant (leaf and stem) has been eliminated. The study on leaf and stem had published for inhibitory activity when diterpenes, triterpenes, and saponin were isolated from an ethanol extract of the leaf and stem as constituents COX - 1 and COX - 2 inhibitory [8]. Polyacetylene and araliadiol were isolated from *A. cordata* ethanol extract. Araliadol has potent cytotoxicity against human breast cardioma cells (MCF - 7) [9]. *A. cordata* leaf and active stem compounds, including oleanolic acid, showed strong anti-nociceptive and anti-inflammatory effects [10].

This study aimed to investigate the bioactive compounds of *Aralia cordata* morphological parts (root, stem, leaf, and blossom) grown in Lithuania (2020). Antioxidant activity and total phenolic concentrations in lyophilized *Aralia cordata* morphological parts ethanol/water mixture (70/30, v/v %) were examined. The antioxidant activity of the samples was tested using the DPPH<sup>•</sup> radical scavenging assay. Higher content of phenolic compounds (2460 mg/100 g) and the highest antiradical activity (122  $\mu$ mol/TE g) had *Aralia cordata* leaf extract., the *Aralia cordata* stem had the lowest content of phenolic compounds (404 mg/100 g) and the lowest antiradical activity (22,16  $\mu$ mol/TE g). This study shows that *Aralia cordata* leaf ethanol/ water extract is a good source of bioactive compounds, possessing strong antioxidant capacity and particular biological activity. It may be assumed that this plant may be attractive for future research objects.

Keywords: Aralia cordata, antioxidant activity, phenolic compounds

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# ENRICHED PLA FILMS WITH ANTIMICROBIAL FACTORS FOR COATINGS AND FOOD PACKAGING

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#### ABSTRACT

Polylactic acid (PLA) is a biopolymer of great interest to the field of food packaging. Compared to widely used polymers (PVC, PET) emerging from petrochemicals, PLA is produced from renewable sources, it is biodegradable and concurrently exhibits mechanical and thermal properties similar to those materials. That makes it an acceptable, environmentally friendlier alternative to food packaging.

Citric acid is a hydroxycarboxylic acid and cobalt Co(II,III) is a transition metal ion, with both of them being important factors in living organisms and exhibiting interesting antimicrobial effects. To that end, metal-organic coordination materials, involving both components, emerge through simple coordination chemistry that could be well-defined in the solid state and solution and capable of delivering antimicrobial properties.

In this work, PLA films and the potential antimicrobial factor (ammonium bis(citrato)cobalt(II), Co-cit) were produced as composite materials for use in food packaging. The solvent casting method was used for preparing films for that purpose. To that end, the emerging reaction mixture is poured into a mould so that the desired film assumes a specific shape and acquires specific thickness as the solvent evaporates. Optimized films in terms of thickness ( $20 \ \mu m$ ,  $50 \ \mu m$ ) and percentage of Co-cit ( $0, 2.5, 10, 20, 30 \ \%$ ) were characterized physicochemically by infrared spectroscopy (FT-IR), and UV-Visible techniques. The rate of release of Co-cit from such films over time was investigated through UV-Visible spectroscopy and the antimicrobial properties in bacterial cultures, most commonly encountered in food, were also perused.

The collective results show that the newly derived films exhibit selective antimicrobial activity toward the bacterium *Listeria monocytogenes* and lay the foundation for the development of a plethora of such films with select organic, inorganic and hybrid inorganic-organic antimicrobial factors and/or mixtures thereof, thus extending the list of antimicrobial properties and the technologically apt materials to be used in food packaging.

Keywords: biopolymer thin films, antimicrobial activity, food packaging, metal-organic factor

#### **INTRODUCTION**

Nowadays, materials commonly used in food packaging include polymers emerging from petrochemicals, such as polyvinyl chloride (PVC) and polyethylene terephthalate (PET) [1]. The reasons for this choice include high availability, low cost and good thermal and mechanical properties. These materials, however, are not biodegradeable and their recycling is very costly due to the fact that they get polluted by food bacteria following their initial use [2]. These two reasons render the aforementioned polymers materials with a negative impact on the environment.

In this work, development of other biocompatible materials enriched with antimicrobial factors in foodstuffs has been sought. For that reason, films of biocompatible materials, such as polylactic acid (PLA), are prepared and enriched with antimicrobial factors. Polylactic acid (PLA) is a thermoplastic with highstrength and high-modulus characteristics [3]. It is also widely used as a biodegradable and renewable plastic [4] with its biodegradability ranging from several months up to two years compared to synthetic polymers [5]. PLA also has better thermal processability compared to other biopolymers and can be processed by extrusion, injection moulding, blow moulding, thermoforming, fiber spinning, and film forming.

Consequently, cognizant of the need to develop new materials with defined antibacterial properties, metal-organics appear to be an apt choice of hybrid composites, with suitable organic components and metal ionic character, collectively contributing to the emergence of biological activity. Among the plethora of transition metal ions present in the periodic table and amenable to chemical reactivity linked to biological action, cobalt is a particularly interesting case due to its biological trace element character and participation in metalloproteins, enzymes and low molecular mass complexes [6-8] important to cellular physiology (e.g. vitamin  $B_{12}$ ). Under appropriately selected conditions, the presence of suitable organic binders facilitates dissolution of Co(II) in physiologically relevant media and promotes retention of its soluble state, thereby projecting complex bioavailable forms that might be useful as antibacterial agents. Promoting formation of the aforementioned forms are physiological metal ion binders, such as citric acid, known for its participation in the energy-producing Krebs cycle in mitochondria. Therefore, synthesis and characterization of such metal-organic complexes emerges as an attractive proposition to the use of atoxic antibacterial agents in food packaging. In light of the aforementioned grounds, synthetically arisen composite PLA-(Cocit) films have been characterized physicochemically by Fourier Transform Infrared Spectroscopy (FT-IR) and their mechanical properties have been tested. The rate at which the potential antimicrobial factor is released from the films is also determined through Ultraviolet-Visible (UV-Visible) spectroscopy. Finally, the films enter antimicrobial activity studies involving typical Gram (+) and Gram (-) food bacteria to assess their biological potential and validate their efficacy as viable materials in food packaging. Driven by the so far evolving work on amtimnicrobilas actively participating in food packaging, we opted to concnetrate on new molecular species that could sustain antimicorbial activity while hosted in an organic acidbased polymer film.

# MATERIALS AND METHODS

#### Materials

All manipulations were carried out under aerobic conditions. The following starting materials were used without further purification.  $Co(NO_3)_2.6H_2O$  was purchased from BDH Chemicals Ltd. Citric acid (C<sub>6</sub>H<sub>8</sub>O<sub>7</sub>) was purchased from Merck-Schuchardt, ethanol chloroform and PLA (L-polylactic acid) were supplied by Sigma-Aldrich.

# **Biocompatible materials**

Certain commonly used biocompatible materials taken into consideration include PLA, poly( $\epsilon$ -caprolactone) (PCL), polyglycolic acid (PGA), and poly(lactic-glycolic acid) (PLGA). Among these materials, PCL is the one with the lowest melting point of 60 °C and also the only one produced from petrochemicals [9]. PGA does not have the same limitations, but it is not easily soluble. In fact, most of the common organic solvents cannot dissolve the polymer [10]. Between PLA and PLGA, PLGA is more expensive and also harder to sythesize since co-polymerization between lactic and glycolic acid is required.

For all of the aforementioned reasons, PLA was chosen for the film preparation. PLA is a biocompatible, biodegradeable material that originates from renewable sources, such as corn

and sugar cane, also exhibiting thermal and mechanical properties very similar to the commonly used polymers PVC and PET [11].

# Antimicrobial factors

Many different potential antimicrobial factors have been synthesized in our Laboratory. Some examples include  $(NH_4)_4[Zn(citrate)_2]$ ,  $(NH_4)_4[Cu(citrate)_2]$ ,  $(NH_4)_4[Ti(citrate)_2]$  and  $(NH_4)_4[Co(citrate)_2]$ . All of these compounds are based on citric acid as a substrate. Citric acid is a hydroxycarboxylic acid participating in key metabolic functions, such as the Krebs cycle, as a physiological substrate. Among all of the above different coordination complexes,  $(NH_4)_4[Co(citrate)_2]$  (Co-cit) has been chosen for this research work. Cobalt is a transition metal present as a cofactor in vitamin B<sub>12</sub>. In such a context, its complex with citric acid, Co-cit, stands as a potential antimicrobial activity factor and as such it was employed in the present work.

# **Physical measurements**

FT-Infrared measurements were taken on a ThermoFinnigan FT-Infra Red IR-200 spectrometer, using KBr pellets. UV-Visible measurements were carried out on a Hitachi U2001 spectrophotometer in the range from 190 to 1000 nm.

**Mechanical Properties**. Tensile strength (TS) and elongation at break (EB) tests were performed at room temperature  $(23 \pm 2 \ ^{\circ}C)$  according to the standard testing method ASTM D882-01. Sample filmswere cut into T-bone shape and three specimens from each film were tested.

# **Materials Preparation**

# Synthesis of $(NH_4)_4[Co(C_6H_5O_7)_2]$

The compound was synthesized according to a slightly modified general procedure outlined in the past [6]. In brief,  $Co(NO_3)_2$ ·6H<sub>2</sub>O (0.30 g, 1.0 mmol) and citric acid (0.42 g, 2.0 mmol) were placed in a 25 mL round bottom flask and dissolved in 5 mL of water. The reaction mixture was stirred at room temperature until both reactants were completely dissolved. The pH was adjusted to 7.0 with ammonia (1.0 M). Subsequently, the reaction solution was filtered and allowed to stand at 4 °C. After a two week period, involving addition of ethanol, dark pink crystals grew out of the solution. The crystalline material was collected by filtration and dried in vacuo. The crystalline material was charactrized by elemental analysis, FT-IR, UV-Visible spectroscopy and X-ray crystallography.

# Film Preparation.

For the production of the composite PLA films enriched with Co-cit, the solvent casting method was used. Chloroform was used as a solvent. The amount of Co-cit added to the reaction mixture was 1, 2.5, 5, 10, 20 and 30% w/w compared to PLA. After all Co-cit had been added, the solution was poured into specific glass moulds and the solvent evaporated. When all of the solvent evaporated, the films were removed from the moulds. The mass of PLA used is such that the produced films after the evaporation have a thickness of 20  $\mu$ m, as shown in Fig. 1.



Fig. 1. Produced PLA film enriched with Co-cit 30% w/w

# **RESULTS AND DISCUSSION**

A series of analyses were conducted to characterize the produced films, test their mechanical properties and examine their antimicrobial activity.

# **Syntheses**

The stoichiometric reaction leading to **Co-cit** is shown below:



$$(NH_4)_4[Co(C_6H_5O_7)_2] + 2(NH_4)NO_3 + 6H_2O$$

# Fourier-transform infrared spectroscopy (FT-IR)

PLA films with no antimicrobial factors and PLA films enriched with Co-cit were analysed through FT-IR spectroscopy. The spectra of the two types of films are shown in Fig. 2.



Fig. 2. FT-IR spectrum for PLA film (blue line) and PLA with Co-cit film (red line)

As can be seen from Fig. 2, the spectrum of PLA does not change substantially upon addition of Co-cit as very similar peaks emerge in both types of films. At 2995 cm<sup>-1</sup>, 1746 cm<sup>-1</sup> and 1080 cm<sup>-1</sup>, peaks are present due to the streching vibrations of  $-CH_3$ , C=O and C-O groups, respectively [12].

#### **Mechanical properties**

The mechanical properties of the generated films were investigated. For this analysis, the ASTM D882-01 standard method was used. According to this method, the films must be cut into a "dog bone" shape of certain measurements so that the tensile properties of the material can be tested [13]. The exact shape is depicted in Fig. 3.



Fig.3. PLA film cut accroding to ASTM D882-01 method

Following the ASTM D882-01, the stress-strain chart for a pure PLA film and an enriched film with Co-cit were determined.

The two films show a similar behavior before breaking. Pure PLA film has a Tensile Strength of 7 MPa while the enriched film has a slighty lower value of 6 MPa. Moreover, the strain before braking for pure PLA film is 0.018 while the strain for the enriched film is 0.015. Finally, the value of Young's modulus E, for pure PLA film is 388 MPa, whereas the enriched film has a slighty higher modulus equal to 444 MPa. All these results show that the enrichment makes the film slightly more brittle. However, the differences between the two films are not major. So, we can safely assume that the enrichment does not really affect the mechanical properties of the film.

## Rate of release of the antimicrobial factor

The amount of time it takes for the antimicrobial factor to be released from the film while soaked in an aqueous medium was also tested with the help of UV-Visible spectrometry. For that reason, films enriched with Co-cit were soaked in ultrapure water for different amounts of time and the absorbance of the water was measured. Absorbance increases over time and reaches a final value at 15 min. The value of absorbance at that time point corresponds to the release of the entire quantity of Co-cit from the film.

# Antimicrobial activity

The antimicrobial activity of the films was studied in vitro. The study was conducted on four types of bacteria commonly encountered in food. Those included two Gram positive bacteria, i.e. *Staphylococcus aureus* and *Listeria monocytogenes*, and two Gram negative bacteria, i.e. *Escherichia coli* and *Salmonella Enteritidis*.

A volume of 100  $\mu$ L of each bacterial culture was spread over the surface of a PCA (plate count agar) plate for testing the films, while another 100  $\mu$ L was spread on a different PCA plate to be used as a control. Next, three sterilized square films, 1 cm<sup>2</sup> each, were placed on the plates in a triangular pattern to maximize the space between them. The three square films had no Co-cit (film E10), 2.5% w/w Co-cit (film E11) and 10% w/w Co-cit (film E12), respectively. All plates were incubated for 24 h at 37 °C. After the 24 h incubation period, any zones of inhibition around the films were measured.

	Inhibition zone radius (mm)			
Bacterium	E10	E11	E12	
Staphylococcus aureus	0.0	0.0	0.0	
Listeria monocytogenes	0.0	6.0	9.0	
Escherichia coli	0.0	0.0	0.0	
Salmonella Enteritidis	0.0	0.0	0.0	

Table 1. Zones of inhibition created by the films against each type of bacteria

As we can see from Table 1, no inhibition zone was created for the bacteria *Staphylococcus aureus, Escherichia coli*, and *Salmonella Enteritidis*. For the bacterium *Listeria monocytogenes*, however, Co-cit does actually create a zone of inhibition, the radius of which increases with the concentration of Co-cit.

## Discussion

Given the nature of the conceived composite material PLA-Co(II) acting as an efficient platform of antimicrobial power in food, the preparation was based on the differential solubility and associated physicochemical properties of PLA and the Co(II)-cit complex.

Film generation was consistent with the following parameters: a) thickness of the film (20  $\mu$ m); b) concentration of Co(II)-cit complex 1 in the film, and c) geometrical circular or square shaped composite samples. All the samples generated under the specified conditions through natural evaporation of the solvent, were examined and were reproducible in all aspects of the parameters outlined. Further characterization of the composite PLA-Co(II) films took place through FT-IR, thus attesting to the retention of the physicochemical properties of the Co(II)-citrate complex embedded in the composite material.

Pursuant to the ultimate goal of the use of such a composite material, monitoring of the release (via UV-Visible) of the Co(II)-citrate complex took place in water, in view of the fact that it is an aqueous medium that the food sample would come in contact with the biopolymeric hybrid film, thereby inducing release of the bioinorganic complex and interacting with the fold ingredients as a potential antimicrobial.

Collectively, the composite PLA-Co(II) material from its inception, design and preparation to the physicochemical characterization, had a well-defined profile justifying its further incorporation in biological experiments perusing the antimicrobial power of the Co(II)-cit agent.

#### CONCLUSIONS

In conclusion, it was possible to produce composite PLA films of different yet defined thickness ( $\geq 20 \ \mu m$ ). A film with a thickness of 20  $\mu m$  was chosen due to the fact that thinner films are better for food packaging. Through enrichment with Co-cit, the composite films showed selective antimicrobial activity only against the bacterium *Listeria monocytogenes*. The enrichment in Co-cit does not affect the mechanical properties of the generated films. Finally, all of the quantity of Co-cit is released after 15 min of soaking in aqueous media. Collectively, it appears that the specific composite film, produced here, exhibits specificity with respect to the bacterium *Listeria monocytogenes*, against which it exhibits antimicrobial activity.

Future goals of the present research include: a) more extensive physicochemicial analysis of the composite materials to investigate their thermal (e.g. TGA) and mechanical properties, b) variably configured composite films of the same base matrial PLA (or mixtures with other polymers) with more diverse still specific antimicrobial properties covering more bacteria (gram positive and negative) in a selective and specific fashion.

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# OPTIMIZATION OF COMMON BUCKWHEAT (FAGOPYRUM ESCULENTUM M.) MULTIENZYME-ASSISTED WATER EXTRACTION AND DETERMINATION OF HYDROPHILICITY

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# ABSTRACT

Common buckwheat (*Fagopyrum esculentum* Moench) are well-known grains for their high nutritional and functional value [1-3]. Moreover, it is found that different types of bioactive compounds and polysaccharides are extracted from common buckwheat. It is rich in flavanoid content, especially rutin, which is able to cause antioxidant activity [4]. Recently, rising demand for higher nutritional value and the 'clean label' trend increased bioactive compounds need in food. Moreover, phenolic compounds found in plant tissues are getting more attention not only for their health-promoting benefits [5–7]. These substances are used as natural food preservatives due to their antioxidant and antimicrobial properties [8,9].

Nevertheless, phenols are found in free and bound [10]. Consistently, phenols have attention regarding their potential to control bacterial virulence and neuroprotective properties [11,12]. Nowadays, enzymatic hydrolysis is used to increase bound phenolics in extracts [2,13]. For grains, the amylolytic and cellulolytic enzymes are common to hydrolyze cellulose, hemicellulose, lignin and pectin, releasing proteins and phenolic compounds. In general, the enzymatic hydrolysis of the cereal matrix leads to the degradation of antinutrients which increase the nutritional value and availability of phenolic compounds, proteins, and carbohydrates [14,15]. Although, phenolic content changes during processing and extraction using enzymes are still in the research field, a connection between parameter variations is missing.

Optimization of Common Buckwheat multienzyme-assisted water extraction is important due to the yield, fermentable sugars, and phenolic compounds for creating higher added value product development. Consistently, liquid and solid fractions are prepared as samples and lyophilized in addition to analysis after extraction. This study was undertaken to find out the optimum multienzymes-water extraction on yield and total phenolic compounds for Common Buckwheat using response surface methodology (RSM). Three independent variables, time (2, 13, and 24 hours), temperature (60 °C, 70 °C, 80 °C), non-starch polysaccharide (NSP) enzymes mixture (0.1, 0.55 and 1.00 ml), were analyzed to optimize the response variables. NSP hydrolyzing enzymes cellulase, xylanase, and  $\beta$ -glucanase were produced by Trichoderma reesei. Estimated optimum conditions for common buckwheat were found: time – 24 hours, temperature – 65 °C, cellulase activity – 8,6 CellG5 Units/ml. For further analysis, different optimization run samples at 70 °C were collected and lyophilized until the hydrophilic property was tested using the water contact angle methodology. Results indicated NSP enzymes activity did not differ between water contact angles after 13 hours of enzymatic water extraction. However, longer fermentation time (24 hours) decreased static water contact angle by approximately  $\theta$  »  $3-7^{\circ}$  for lyophilized water extract and  $\theta$ »  $2-7^{\circ}$  for solid fraction after fermentation. It implies enzymatic hydrolysis during water extraction increased hydrophilic properties in solid fraction and decreased hydrophilicity in water fraction due to the enzymes cleaves glycosidic bonds releasing water-soluble compounds.

**Keywords:** Common buckwheat, enzyme-assisted water extraction, optimization, hydrophilicity, non-starch polysaccharide enzymes, *Trichoderma reesei* 

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# OPTIMIZATION OF CONDITIONS FOR BEE POLLEN LACTIC ACID FERMENTATION

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#### ABSTRACT

Bee pollen is one of the most well-known apitherapeutic product, whose chemical composition is considered as a source of biologically active substance, which is maintain as the main reason for its antioxidant and antibacterial properties. Due to the pollen wall, bee pollen is not digestible in the body and some useful compounds cannot be absorbed, therefore it is recommended to treat the product accordingly – to ferment. The aim of this study was to optimize bee pollen fermentation conditions. Bee pollen from Lithuania was fermented. Spontaneous fermentation and fermentation with *L. rhamnosus* were applied on bee pollen keeping prepared samples for 2, 4, 8, 12, 16 and 20 days, respectively. Total phenolic compound content, total flavonoid content, antioxidant activity by spectrophotometric methods, antibacterial activity of diffusion method on agar and changes of pH were determined in the fermented bee pollen extracts in order to optimize fermentation process conditions. Results were evaluated employing chemometric analysis methods, which included differential equations and data approximation. The optimal duration of fermentation was determined finding the extremum as a function to observed of the highest total phenolic content, total flavonoid content, total flavonoid content compounds, antioxidant and antibacterial activity in the samples. According to the results, the optimal duration of fermentation are 9 days using *L. rhamnosus* and 11 days for spontaneous fermentation.

Keywords: bee pollen, fermentation, optimization, chemometric analysis

# **INTRODUCTION**

Honeybee (lot. *Apis mellifera*) is one of the most wonderful insects in the world. These insects play a major role in pollination for the production of plants, fruits, vegetables, their seeds and maintain the biodiversity [1]. Also, the honeybees collect pollen and are responsible for the production of honey, propolis, bee-bread, beeswax, and royal jelly, which are used as a food source not just for bees, but also for other animals and as health promotion remedies for humans [2].

During the last few years, interest in the apitherapy products has been increased rapidly. More and more apiculture products are considered as a functional food, which mediate a variety of biological effects: improve immunity system and also have antioxidant, antimicrobic, anti-inflammatory, anti-atherosclerotic, hepatoprotective or anticarcinogenic activities. According to the researches, these properties are determined by bioactive and nutrition compounds as proteins, carbohydrates, nucleic and amino acids, phytosterols, polyphenols, sugars or minerals [3, 4]. Bee pollen is one of the most assessed natural apitherapeutic products, which is characterized by previously mentioned properties.

Bee pollen is a powdery substance grain, as a result of flower pollen agglutination, which are collected by worker honeybees using nectar or honey and bees' secreted gland with enzyme. This natural product is considered as one of the main sources of bioactive compounds, lipids, proteins, carbohydrates, vitamins, fatty acids, carotenoids and depends on the bee pollen geographical and botanical origin [5]. Bee pollen cells have a specific cell wall, which is known as the exine and is made from strong, elastic sporopollenin [6]. This cell wall influenced limited availability for humans, because it is difficult to digest it in the stomach and a large amount of useful compounds are not absorbed. The aim is therefore to find a better way to improve its

bioavailability. One of the recommended ways to destroy the wall of bee pollen cell is to use lactic acid fermentation and increase nutritional and bioactive compounds. Fermentation of bee pollen has been studied by Salazar-Gonzalez and Diaz-Moreno (2016), Kaškonienė with colleagues (2018, 2020) and Zuluaga with colleagues (2015). According to the published data, a positive effect of fermentation to bee pollen antimicrobial and antioxidant activities, and increase of biologically active compounds was determined. The aim of this research was to optimize the lactic acid fermentation conditions of bee pollen using chemometric analysis methods. The obtained data will help to properly determine the best fermentation conditions to obtain the maximum amount of biologically active compounds.

# MATERIALS AND METHODS

#### **Bee pollen sample**

Polyfloral bee pollen sample was collected in Kuršėnai region, Lithuania (55°59'N 22°55'E). Dried sample was stored in a refrigerator at 6 °C for a maximum of four weeks until analysis. Sample was homogenised with a pestle and porcelain mortar before analysis and extracts preparation procedure.

# Solid-state fermentation

Bee pollen samples were fermented using solid-state fermentation using the method described in Kaškonienė et al. (2020). In this study was performed spontaneous fermentation and bacterial fermentation using *L. rhamnosus* lactic acid bacteria culture. An inoculum of *L. rhamnosus* GG (ATCC 53103) (Gefilus, Valio Ltd., Helsinki, Finland) was prepared in MRS broth with Tween 80 (Biolife Italiana S.r.l). Bacteria was grown statically at 37 °C, until optical density reached 0.730, which was determined spectrophotometrically using a Spectronic 1201 spectrophotometer (Milton Roy Co., Frederick, Maryland, USA) at 600 nm. This optical density corresponded to  $2.9 \cdot 10^9$  CFU/ml, which was calculated using growth curve [8].

10 grams of fresh bee pollen was moistened with 2 mL of bidistilled water and left for 2 hours. Mixture of 1.5 g of honey (collected mainly from dandelion, rape and linden) and 2.5 mL water were heated to boiling using a LBX H03D heater (Labbox, Barcelona, Spain), cooled down and added into the swollen bee pollen. Then, to perform bacterial fermentation, 800  $\mu$ l of *L. rhamnosus* 2.9 · 10<sup>9</sup> CFU/ml was added to the half of the samples, and the remaining part of the samples was mixed with 800  $\mu$ l MRS broth with Tween 80 (Biolife Italiana S.r.l) to implement spontaneous fermentation. Bioprocess was done in 10 mL vials leaving about 10% of vial space. Samples were placed into an incubator (Biosan, Riga, Latvia) for fermentation at 37 °C for 2, 4, 8, 12, 16 and 20 days.

#### **Extracts preparation**

One gram of fermented and natural bee pollen samples were extracted with 10 mL of 80% methanol (Sigma-Aldrich, Taufkirchen, Germany) for spectrophotometric and antibacterial analysis and with 7.5 mL of bidistilled water for pH measurements for 24 h in an orbital shaker "Titertek" (Flow Laboratories, Meckenheim, Germany) at 180 rpm. Methanolic extracts were filtered through 7-10  $\mu$ m paper filter (Labbox) and repeatedly filtered with a 0.22  $\mu$ m polyvinylidene fluoride (PVDF) membrane filter (BGB Analytik, Alexandria, Virginia, USA). Distilled water-based extracts were filtered through a 0.45  $\mu$ m polyvinylidene fluoride (PVDF) membrane filter (BGB Analytik, Alexandria, Virginia, usandria, Va, USA). Obtained samples stored in a refrigerator at 4 °C for a maximum of 2 weeks [8, 10].

#### pH measurement

The pH-meter UltraBasic Benchtop UB-10 (Denver Instrument Company, Denver, CO, USA) combined with glass electrode was used to measure the pH of water-based bee pollen extracts.

#### Spectrophotometric tests

Spectrophotometrically total phenolic compound content, total flavonoid content and radical scavenging activity were determined in fermented and nonfermented bee pollen samples according to the methods described in Adaškevičiūtė et. al. (2019). Total phenolic compounds content was estimated by the Folin-Ciocalteu, total flavonoid content was determined according to colorimetric aluminium trichloride reaction and radical scavenging activity was evaluated using 1,1-diphenyl-2-picrylhydrazyl (DPPH) free radical. All results were expressed as milligram rutin equivalent (RUE) per gram of sample.

#### **Evaluation of antibacterial activity**

Antibacterial activity of fermented and natural bee pollen extracts was done by agar well diffusion method. The inhibition of growth of three bacteria, namely *Staphylococcus aureus*, *Listeria monocytogenes* and *Salmonella enteritidis*, of fermented and natural bee pollen extracts samples were evaluated. Indicator strains were revitalized before the experiment using LB medium (Carl Roth, Karlsruhe, Germany). The optical density of the bacterial inoculum in 0.9% NaCl solution were spectrophotometrically adjusted to 0.100 at 625 nm. Then 100  $\mu$ l of this suspension was poured into flask with 100 mL LB agar and incubated at 37 °C for 24 h. Before the antibacterial analysis, 100  $\mu$ l of overnight suspension was poured into flask with 100 mL freshly autoclaved LB agar and was spilled out into Petri dishes.

Five 10 mm diameter wells were cut into the agar using a sterile cork borer. The bottom of the well was covered with a drop of liquid agar to prevent extract leakage. 100  $\mu$ l of each extract was added into three wells, the other two were filled with 100  $\mu$ l 80% methanol and 0.9% NaCl, respectively. Plates were incubated at 37 °C for 24 h. The clear zone (in mm) around the well was measured using a ruler (resolution  $\pm$  0.5 mm). The inhibition zone (IZ, mm) was calculated according to the formula:

$$IZ = \frac{D-d}{2},\tag{1}$$

where D is the diameter of the clear zone around the well, in mm; d is the well diameter, in mm.

Ceftazidime (CEF) was used as a standard antibacterial drug. Solutions with different concentration (3-60  $\mu$ g/ml) of ceftazidime pentahydrate (98%; Acros Organics, Gel, Belgium) were used for preparation of the calibration curve. Antibacterial activity of bee pollen extracts were expressed in  $\mu$ g CEF equivalents/ml.

#### Statistical analysis

"MS Excel 15.11" (2015, Microsoft, USA) software was used to perform chemometric analysis. The data set representing optimal duration of bee pollen fermentation was composed from one sample, when it was described by four variables (total phenolic content, total flavonoid content, radical scavenging activity and antibacterial activity) measured ten times. According to the received values of each variables differential calculations was performed. Firstly, the obtained measurements were approximated and interpolated. According to the received dependencies, derivatives were made and curves were drawn. Based on the curves, maxima were determined and optimal duration of fermentation was established.

#### **RESULTS AND DISCUSSION**

Sample of natural bee collected pollen was fermented using *L. rhamnosus* and without the addition of bacteria (called spontaneous fermentation in the text below). The optimization of fermentation duration was evaluated by comparison of the properties obtained after 2, 4, 8, 12, 16, 20 days of fermentation. This study did not involve evaluation of the botanical origin of the tested sample.

Above all, pH changes were evaluated in spontaneously and with *L. rhamnosus* fermented bee pollen samples. The variation of the results is shown in Fig. 1. According to the results, pH significantly decreased ( $p \le 0.05$ ) when fermentation time was increasing. It was determined that pH varied from  $5.16 \pm 0.02$  before fermentation to  $4.61 \pm 0.01$  after 20 days fermentation. At the end of bioprocess, microorganisms produce organic acids and increase amount of acids in the medium, therefore pH is decreasing. This process prevents from the growth and development of pathogenic bacteria [13]. Scientists from India also determined that different durations of sunflower pollen fermentation with *Lactobacillus lactis* bacterial culture predestined decreasing of pH. According to their results, the content of lactic acid has changed from 4.1% to 6.1% after 7 days of fermentation and pH reduced from 6.5 to 4.0-4.2 after bioprocess [14].





The results in Fig. 1 shows that bacterial fermentation revealed lower pH than spontaneous fermentation. This may be explained by the ability of lactic acid bacteria to secrete an appropriate amount of lactic acid during the process [15]. However, the results also reflect the fact that after reaching a certain optimal fermentation time, the changes of pH during increasing of fermentation duration becomes minimal, which allows to assume that organic acids are no longer produced, and the bioprocess stopped.

The optimization of bee pollen spontaneous and bacterial fermentation duration was performed by evaluating the total phenolic content, total flavonoid content, radical scavenging activity and antibacterial activity against *L. monocytogenes*, *S. enteritidis*, *S. aureus* bacteria.

After fermentation of different duration by days, total phenolic content in bee pollen samples were evaluated using Folin-Ciocalteu colorimetric method. According to the results it was determined that total phenolic content increased by 1.1-1.7 times ( $p \le 0.05$ ) after fermentation. The highest total phenolic content was established after 12 days of spontaneous fermentation (22.30 ± 0.09 mg/g (RE)) and after 8 days of bacterial fermentation (22.13 ± 0.11 mg/g (RE)). Based on the obtained results it is assumed that the additional culture of lactic acid bacteria accelerates the fermentation process and promotes the decomposition of pollen cell walls and faster release of biologically active substances.

Evaluation of amount of total flavonoid compounds after bee pollen fermentation over different duration of bioprocess was performed using aluminium (III) chloride method. Based on the derived results it was assessed that total flavonoid content increased from  $5.59 \pm 0.03$  to  $7.80 \pm 0.02 \text{ mg/mg}$  (RE) (p  $\leq 0.05$ ). The highest total amount of flavonoids was found after the same durations of fermentations as the total amount of phenolic compounds: after spontaneous fermentation is obtained after 12 days ( $7.80 \pm 0.02 \text{ mg/g}$  (RE)) of bioprocess and after bacterial fermentation – after 8 days ( $7.05 \pm 0.02 \text{ mg/g}$  (RE)). The results of total phenolic compounds content strongly correlated with total flavonoid content (r = 0.955). The obtained results are comparable with other researches: it was determined that total flavonoid content after bacterial fermentation and spontaneous fermentation differs slightly [9].

An increase of radical scavenging activity by 1.2-2.4 times of bee pollen samples was observed. The correlation coefficient estimated between the radical scavenging activity and the total phenolic content was r = 0.909 ( $p \le 0.05$ ). The highest radical scavenging activity was determined after 12 days of spontaneous fermentation (14.54  $\pm$  0.02 mg/g (RE)) and after 8 days of bacterial fermentation (15.00  $\pm$  0.01 mg/g (RE)). The strong correlation of total phenolic content and radical scavenging activity shows that after fermentation bee pollen cell walls are damaged and more biologically active substances are released.

The antibacterial activity of the bee pollen samples before and after fermentation against three types of pathogenic bacteria (*L. monocytogenes*, *S. enteritidis*, *S. aureus*) was determined and compared with the activity of CEF. Experimental results show that antibacterial activity was strongly related to duration of fermentation. Antibacterial activity against *S. enteritidis* after fermentation increased from  $27.60 \pm 2.12$  to  $57.84 \pm 2.26 \ \mu g/ml$  (CEF), against *L. monocytogenes* - from  $24.25 \pm 1.30$  to  $55.04 \pm 1.30 \ \mu g/ml$  (CEF), against *S. aureus* - from 8.06  $\pm 1.84$  to  $35.36 \pm 1.57 \ \mu g/ml$  (CEF). The highest antibacterial activity was determined after 12 days of spontaneous fermentation ( $57.84 \pm 2.26 \ \mu g/ml$  (CEF) against *S. aureus*) and 8 days of bacterial fermentation ( $56.96 \pm 2.27 \ \mu g/ml$  (CEF) against *S. aureus*) and 8 days of bacterial fermentation ( $56.96 \pm 2.27 \ \mu g/ml$  (CEF) against *S. aureus*).

Based on the changes of evaluated criteria, the determination of the optimal fermentation duration was performed according to the obtained and previously described results of total phenolic content, total flavonoid content, radical scavenging and antibacterial activities. First of all, approximate functional dependencies crossing all experimental points was identified for each parameter and their derivatives was deduced accordingly. According to the equation of each parameter after interpolation, functions derivative curves was drawn for bacterial and spontaneous fermentation (Fig. 2, Fig. 3).



Fig. 2. Determination of the optimal duration of spontaneous fermentation using interpolation (F(AA) – variation of total phenolic content, total flavonoid content and radical scavenging activity in mg/g (RE) per days, F(AB) – variation of antibacterial activity in µg/ml (CFE) per days)



Fig. 3. Determination of the optimal duration of bacterial fermentation using interpolation (F(AA) – variation of total phenolic content, total flavonoid content and radical scavenging activity in mg/g (RE) per days, F(AB) – variation of antibacterial activity in µg/ml (CFE) per days)

Optimal duration of fermentation was determined according to derivative curves when the function of derivative curves, corresponding parameter, reaches the extremum – relative maximum or minimum. A relative maximum point corresponds where the function changes direction from increasing to decreasing, therefore in this study where the curves cross coordinate axis of x. The necessary derivation of functional dependencies of total phenolic content, total flavonoid content, radical scavenging activity and antibacterial activity parameters after fermentation were performed and the results showed that the optimal duration of bee pollen spontaneous fermentation is 11 days and for bacterial fermentation -9 days. The reason for the shorter bacterial fermentation duration can be considered of the ability of the added lactic acid bacteria to secrete lactic acid and influence lower the pH. The higher lactic acid content results determined faster formation of products and shorter process flow due to increased inhibition of bacterial growth and thus reduced process speed and scale [16, 17]. To our knowledge, this is the first study of duration of bee pollen fermentation optimization.

# CONCLUSION

Solid-state fermentation of the bee pollen has a positive effect on its antioxidant activity and antibacterial activity. Differential calculations revealed that the optimal duration of bacterial fermentation are 9 days using *L. rhamnosus* lactic acid bacteria culture and 11 days for spontaneous fermentation. Additional optimization studies may be required to use other strains of lactic acid bacteria for fermentation.

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# **CONFERENCE PAPERS**

# III.5. Plant biology and physiology

NEXT-GENERATION TOMATOES SOLANUM LYCOPERSICUM CV. MICRO-TOM 1108
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SCREENING AND QUANTITATIVE DETERMINATIONS

# THE BIOCHEMICAL CHANGES OF LIGHT-STRESS EFFECTS IN NEXT-GENERATION TOMATOES SOLANUM LYCOPERSICUM CV. MICRO-TOM

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#### ABSTRACT

Tomato is one of the most popular and important plants worldwide, so studies examining various effects of light on tomato growth are gaining an importance. Our study aimed to determine how lightstress effects are transferred to the next-generation of Solanum Lycopersicum cv. Micro-Tom. Plants (F0 generation) were grown under such light-emitting diode (LED) conditions:  $R_{F0}$  (100% 660 nm),  $RB_{F0}$  (75% 660 nm, 25% 445 nm),  $RBFR_{F0}$  (60% 660 nm, 20% 445 nm, 20% 731 nm). Seeds were collected in XII organogenesis stage (809 BBCH-scale). Plants of the F1 generation were grown under high-pressure sodium (HPS) lighting (R<sub>F1</sub>; RB<sub>F1</sub>; RBFR<sub>F1</sub>). During both experiments, 250 µmol m<sup>-2</sup> s<sup>-1</sup> photosynthetic photon flux density (PPFD), 16 h photoperiod, +19/23° C temperature, and 60% air humidity were maintained. The samples of soluble sugars, phytohormones, and phenolic compounds were collected at the end of the experiment. Compared to other lighting treatments, RBFR resulted in a significant decrease of glucose and fructose, but a significant increase of abscisic and jasmonic acids and m-coumaric acid accumulation in F0 generation was observed. However, lighting conditions applied for F0 tomato plants had no significant effects on abscisic acid, jasmonic acid or m-coumaric acid accumulation in F1 generation, except of hexoses. The PCA score scatterplot indicates that the responses of F0 generation were distinct from the responses of F1 generation to lighting conditions. Besides, the response of stress hormones, abscisic acid and jasmonic acid, was clearly distinct from m-coumaric acid and hexoses.

Keywords: Soluble sugars, phytohormones, m-coumaric acid, light stress

# **INTRODUCTION**

Light is an essential factor for plant growth in closed environment chambers and might be used as a stress factor [1]. Current growth tehnologies focus on economic viability, so low power consumption and high yield lead to the use of fixed wavelengths low power lightemitting diode (LED) light systems [2]. Still, the long term effect on plants is not fully understood. Plant epigenetics is unique because it can be passed down from generation to generation directly and enable faster adaptation to changed environmental conditions than genetic mutations [3].

The tomato is the most popular vegetable in the world. It has multiple mutants who have different characteristics, so a lot of studies focus on tomato plants growth, physiology ,and genomes. Micro-Tom is a dwarf tomato cultivar (*Solanum Lycopersicum* L.) has been used as a plant model for studies of light effects on shor-term biochemical response. The stress memory can be retained for long or short durations if it depends on stress-induced histone modifications, DNA methylation, or proteins, RNAs, and metabolites respectively [4]. Epigenetic modifications can regulate gene expression without provoking any changes in the genomic DNA sequences. On the other hand biochemical signals may also alter the epigenome and the transduction of modifications to control the downstream epigenetic pathways [5]. The tight connection between epigenetic regulation and plant hormone (auxin, asmonic acid, absicic acid) signaling was explained in many studies [6,7] Abscisic acid is a plant phytohormone who have a mayor role in plant defense against all main environmental stress factors, [8]. The primary

function of jasmonic acid (JA) and its various metabolites is to regulate plant responses to abiotic and biotic stresses, as well as plant growth and developmental processes such as growth inhibition, aging, and development. [9]. Plants also use light signaling pathways to defend plants vital functions. Phytochromes modulate plant stress hormone signaling such as ABA and JA and the direct involvement of PIF4 / PIF7 in activating CBF genes. These PIFs can act directly on CBF promoters to induce gene expression that improves cold tolerance. In contrast to moderate to high temperatures (e.g., 28 ° C for Arabidopsis). [10]

Phenols are secondary metabolites with a wide variety. Phenols accumulate in plant cells as substances for the fight against stressors: intense light, low temperatures, pathogens, nutrient deficiencies [11].

Light effect on phenotype is well known, red LED can make plants go longer and thinner [12]. blue light inhibits growth; plants grow under blue light, usually shorter and smaller, thicker and darker green leaves [13]. The main effect of the far red light on a plant is the growth increase and swelling, FR increases the leaves and stem. Illuminating plants with different wavelengths of light may cause a long-lasting plant response [14]. We focused on the main light components (blue, red, and far-red), which trigger photosynthetic and photomorphogenetic plant receptors [15] to test how the light stress will affect the short-term biochemical response and if these changes will be transferred to the next generation.

# METHODOLOGY

Plant cultivation and lighting conditions. The plants were grown in closed environment chamber under controlled conditions. Tomatoes are seeded into the prepared peat substrate pH (60% H<sub>2</sub>O) 5.5-6.5, average content of macro and microelements mg / 1-1.,N - 110, P<sub>2</sub>O<sub>5</sub>- 50, K<sub>2</sub>O - 160, Ca - 242, Mg - 29.5, S - 212, Fe - 1.7, Mn - 0.5, Cu - 31, B - 2, Zn - 1.6. and grown in optimal condintion for micro tom - 16 h day and 8 h night photoperiod,  $+23/19 \pm 2^{\circ}$ C temperature, 60% air humidity was maintained. After a 3 weeks, the tomato transplants are transferred to 1.5-liter pots, and 8 plants was placed in trays. 7 days after transfer , growth fertilizers was used (NO<sub>3</sub>2,0%, NH<sub>4</sub>0,6%, P<sub>2</sub>O<sub>5</sub>1,1%, K<sub>2</sub>0 3,1%) (Plagron "Terra grow").When flowers wereformed, fertilizers for flowering and fruiting were used (NO<sub>3</sub>1,6%, NH<sub>4</sub>0,5%, P<sub>2</sub>O<sub>5</sub> 1,6%, , K<sub>2</sub>0 3,9%) (Plagron "terra blom"). Plants were watered every few days. The fertilizer ratio is 1ml fertilizer to 500ml watter.

Plants (F0 generation) were grown under light-emitting diode (LED)conditions:  $R_{F0}$  (100% 660 nm),  $RB_{F0}$  (75% 660 nm, 25% 445 nm),  $RBFR_{F0}$  (60% 660 nm, 20% 445 nm, 20% 731 nm) (table 1). Seeds from 8 plants were collected in XII organogenesis stage (809 BBCH-scale).8 plant per experiment of F1 generation was grown under high-pressure sodium (HPS) lighting ( $R_{F1}$ ;  $RB_{F1}$ ;  $RBFR_{F1}$ ). During both experiments 250 µmol m<sup>-2</sup> s<sup>-1</sup> photosynthetic photon flux density (PPFD) was maintained.

Light source	~500-680 nm	660nm	445nm	731nm
HPS	100%			
R		100%	75%	60%
R+B			25%	20%
R+B+FR				20%

Table 1. Experimental setup for first tomato generation.

For one biochemical analysis 0.5g of tomato leaves, a total of 3 samples per single analysis were frozen in liquid nitrogen and stored at -32  $^{\circ}$  C until analysis.

Determination of m-coumaric acid. Frozen plant mass was homogenized in a ceramic mortar and diluted with 4 ml of methanol 80%. After 24 hours, the extract was filtered through a a 0.2  $\mu$ m pore diameter cellulose membrane filter. The samples were stored in a freezer at -18 ° C until analysis. Analysis by high-performance liquid chromatography was performed using a Shimadzu 10A HPLC system with a refractive index detector (Shimadzu, Japan) and a NUCLEODUR Sphinx RP 5 column (150mm x 4mm). The column was thermostated and maintained at 40 ° C. Mobile phase: 99.9% acetonitrile. Flow rate: 1 ml min<sup>-1</sup>. Injection volume: 10  $\mu$ l. Wavelength 280 nm. Three analytical replicates were performed. m-coumaric acid will be evaluated according to the equation of the calibration regression curve.

Phytohormone determination. Approximately 0.5 g of fresh leaf tissue was ground with liquid  $N_2$  and extracted with 5 ml of cold 50% (v/v) acetonitrile. An internal standard solution mixture containing isotope-labeled phytohormones (100 pmol ABA, and 100 pmol JA) was added to the samples. Samples were purified using Chromabond HLB SPE cartridges (3 ml, 60 mg, MachereyNagel). Briefly, cartridges were conditioned with 2 ml MeOH and 2 ml H<sub>2</sub>O. Sample elution was carried out with 30% acetonitrile, and each eluted sample was collected together with the pass-through. Samples were dried in a vacuum concentrator and dissolved in 50 µl of 30% (v/v) acetonitrile. Phytohormone analysis was performed using ultra performance liquid chromatography (UPLC; Waters) combined with mass spectrometry (LC-MS/MS). Separation of phytohormones (JA, ABA,) was performed using an Acquity BEH C18 column ( $1.0 \times 150$ mm; Waters). The mobile phase was A: water [with 0.02% (v/v) acetic acid], and B: acetonitrile with 0.02% (v/v) acetic acid, at a flow rate of 0.1 ml min-1. Gradient was maintained at 5% B for 3 min, raised to 40% B in 12 min, raised to 90% B in 1 min, maintained at 90% B for 1.5 min, and equilibrated at 5% B for 4 min, before starting the next injection. Hormones were detected with the Bruker Ultra HTC ion trap mass spectrometer in negative mode, using multiple reaction monitoring (MRM)

Soluble sugar determination. Frozen plant tissues were homogenized in a ceramic mortar and diluted with 2 ml of deionized water. And put into sharker on low speed at 4h, centrifuge on 12 000g for 15 min, take 0.5 supernatant and 0.5 0.01% acetonitrile, was put in to cooler for 30 min and extract was filtered through a cellulose filter, before analysis sample was filtered through a 0.2  $\mu$ m pore diameter membrane cellulose filter. The samples are stored in a freezer at -18 °. Analysis by high-performance liquid chromatography was performed using a Shimadzu 10A HPLC system with a refractive index detector (Shimadzu, Japan) and an Zorbax Extend C18 2.1x100 mm column The column was thermostated and maintained at +35 ° C. Mobile phase: A: water with 0.02% Acetic acid and B: Acetonitrile with 0.02% Acetic acid. Gradient from 5% B to 80% B. Flow rate: 0.4 ml / min. Injection volume: 10  $\mu$ l. Three analytical replicates were performed. Sugars were quantified from the equation of the calibration

Statistics - ANOVA (ANalysis Of VAriance) were performed using the Xlstat 2020 computational environment using built-in functions. Analysis of variance (ANOVA) was carried out along with the Tukey's HSD test for statistical analyses. Differences were considered to be significant at p < 0.05.

# **RESULTS AND DISCUSSION**

Compared to other lighting conditions, the content of ABA was significantly lower under HPS lighting in tomato leaves of F0 generation (Table 2). RB lighting significantly reduced the accumulation of JA compared to RBRF treatment. In some studies FR is used to suppress jasmone acids [16].Significant increase of mCA was observed under HPS and RBFR lighting, some plants like *Verbena officinalis* mCA concentration not affected by light sources [17]. HPS resulted in the significant increase of hexoses, while RBFR led to the significant decrease compared to R or RB lighting. The result is the opposite on a team that used white light + FR

and seen an increase in soluble sugars [16], and young tomato seed leaf to show increase soluble sugars in RB[18]. However, lighting conditions applied for F0 tomato plants had no significant effects on ABA, JA or mCA accumulation in F1 generation. Meanwhile, the same tendency of hexoses accumulation was observed in both generations. Moreover, fructose and glucose accumulation showed the significant response in all lighting treatments comparing F0 and F1 generations. RBFR resulted in not significant response of ABA and JA, while R or RB lighting showed the insignificant response of mCA.

Hexoses - HPS resulted in a significant increase of hexoses, while RBFR led to a substantial decrease. The result is the opposite on a team that used white light + FR and seen an increase in soluble sugars [16], young tomato seed leaf to show increase soluble sugars in RB [18].

	ABA	JA	mCA	Fru	Glu	
	$(\mu g g^{-1})$	$(\mu g g^{-1})$	$(mg g^{-1})$	$(mg g^{-1})$	$(mg g^{-1})$	
F0 generation						
HPS	3.12a	1.45ab	0.05b	3.88b	3.94b	
R	8.42b	1.82ab	0.02a	3.34ab	3.34ab	
R+B	8.00 b	0.99a	0.01a	3.57ab	3.50ab	
R+B+FR	6.73b	2.69b	0.04b	2.25a	2.29a	
	F1 generation					
HPS	4.53a	0.99a	0.05a	4.13b	3.70ab	
R	6.75a	1.12a	0.05a	2.89b	3.23a	
R+B	4.94a	1.19a	0.05a	3.95ab	4.88b	
R+B+FR	3.98a	0.77a	0.05a	2.65a	2.72a	
F0 x F1 generation						
HPS	а	а	а	а	а	
R	a	a	ab	a	a	
R+B	a	a	ab	a	a	
R+B+FR	ab	ab	а	a	a	

Table 2. The effect of light conditions on primary and secondary metabolites content in tomato leaves in F0 and F1 generations.

F0 plants grew under blue (B. 455 nm). red (R. 660 nm). far-red- (FR. 731nm) LED combinations or high-pressure sodium (HPS) lighting at 16 h photoperiod. PPFD - 250  $\mu$ mol m<sup>-2</sup> s<sup>-1</sup>. F1 plants grew under HPS lighting at 16 h photoperiod. PPFD - 250  $\mu$ mol m<sup>-2</sup> s<sup>-1</sup>. F1 plants grew under HPS lighting at 16 h photoperiod. PPFD - 250  $\mu$ mol m<sup>-2</sup> s<sup>-1</sup>. The data were processed using XLStat software. the Tukey (HSD) test at the confidence level p = 0.05 (biological replicates. n=3). ABA – abscisic acid. JA – jasmonic acid. mCA – mcoumaric acid. Fru – fructose. Glu – glucose. Epigenetic response between generations – A mean no significant difference between concentartions in F0 and F1 generation significant, AB – significant difference between concentartions.

Strong positive correlation was found between fructose and glucose, meanwhile strong negative correlation between ABA and mCA indicates their opposite action model to stress conditions (Table 3).

Variables	JA	mCA	Fru	Glu
ABA	0.206	-0.691	-0.107	-0.164
JA		-0.187	-0.323	-0.313
mCA			0.002	0.129
Fru				0.890

Table 3. Correlation between primary and secondary metabolites and lighting conditions.

PCA score scatterplot (Fig. 1) shows the average coordinates of abscisic acid, jasmonic acid, m-coumaric acid, fructose and glucose in tomato leaves under blue, red, far-red combinations or HPS lighting in F0 and F1 generations. The first two factors (F1 vs. F2) of the PCA, explained 76.30 % of the total variance in the lighting conditions response. F1 explained approximately 32 %, whereas F2 explained 44.9 % of the total variability. In terms of F2 score, the responses of F0 generation were distinct from the responses of F1 generation to lighting conditions. The response of stress hormones, ABA and JA, was clearly distinct from m-coumaric acid and hexoses.



Figure 1. The PCA scatterplot analysis in tomato leaves, indicating distinct differences in metabolites depending on lighting conditions.

F0 plants grew under blue (B. 455 nm). red (R. 660 nm). far-red- (FR. 731nm) LED. or high-pressure sodium (HPS) lighting at 16 h photoperiod. PPFD - 250  $\mu$ mol m<sup>-2</sup> s<sup>-1</sup>. F1 plants grew under HPS lighting at 16 h photoperiod. PPFD - 250  $\mu$ mol m<sup>-2</sup> s<sup>-1</sup>

# CONCLUSSIONS

Compared to other lighting treatments, RBFR resulted in a significant decrease of glucose and fructose, but a significant increase of abscisic and jasmonic acids and m-coumaric acid accumulation in F0 generation was observed. However, lighting conditions applied for F0 tomato plants had no significant effects on ABA, JA or mCA accumulation in F1 generation, except of hexoses. The PCA score scatterplot indicates that the responses of F0 generation were distinct from the responses of F1 generation to lighting conditions. Besides, the response of stress hormones, ABA and JA, was clearly distinct from m-coumaric acid and hexoses. The biochemical changes of light-stress effects in next-generation tomatoes *solanum lycopersicum* cv. Micro-tom was observed.

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# **EFFECTS OF PH BUFFERED NUTRIENT SOLUTION ON HYDROPONICALLY GROWN PLANTS: A REVIEW**

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#### EXTENDED ABSTRACT

Plant mineral nutrition is directly dependent on the pH of the nutrient solution, optimal levels usually ranging from 5.5 to 6.5 for hydroponic growth [1]. Nutrient solution used in hydroponics has a low buffering capacity, therefore, slight increase of H<sup>+</sup> or OH<sup>-</sup> ions will alter nutrient solution pH [2]. Depending on the growth phase plant will uptake more cations or anions, therefore, root zone pH levels will fluctuate. pH fluctuation above or below desired range will decrease efficiency of mineral nutrition, limiting plant productivity [3, 4]. pH changes of nutrient solution can be actively, commonly used method, controlled with titrating (strong acid or base) agent or passively regulated using buffers or ion exchange resins [5-7]. Hydroponic growth potential can be maximized if nutrient solution pH is maintained at optimal interval. **Our objective** was to evaluate nutrient solution buffer capacity using Henderson-Hasselbalch (1) equation and make literature review on pH management possibilities with artificially increased nutrient solution buffer capacity for easier and more precise hydroponic growth.

$$= pka + \log\left(\frac{\lfloor A \rfloor}{\lfloor HA \rfloor}\right)$$

Calculated modified Hoagland's nutrient solution buffer capacity (2) is 0.63 mM, therefore, pH mitigation ability is very limited.

рН

r 4-3

$$\beta = \frac{10[HA] - [A^-]}{11} \tag{2}$$

Plant physiological requirements limits maximum buffer capacity which can be reached with supplemental buffering agents [8]. Reviewed literature implies that sufficient buffering of nutrient solution could be reached at 1 - 10 mM zwitterionic buffer concentration [6,9]. Highest buffer capacity is reached when pK<sub>a</sub> is equal to pH.

Keywords: Hydroponics, pH, buffer, buffering capacity

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# INCREASING THE OVERALL RESISTANCE OF LITHUANIA MAIN FOREST TREE SPECIES TO PATHOGENS BY THE INNOVATIVE COMBINATION OF GENETIC AND PHYSICAL METHODS

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## **EXTENDED ABSTRACT**

There are many factors which are related to stands structural properties in forest ecosystems [1]. Climate change has affected forest ecosystems over the world and temperature changes have direct and indirect impact on forest health. One of the most urgent problems appeared due to climate change is faster spread of pathogens which have disastrous consequences for tree diseases and stability of ecosystem functioning. Pest outbreaks have extremely negative influence on forest environment, human health and economy, especially in large forest areas [2;3]. Scientists try to find anticipatory strategies, which would be used on purpose to predict pest outbreaks in forests before the outbreaks start and create tools to increase tree itself protection [4;5;6]. Forest tree resistance against pathogens is related to tree vitality, its energy of growth and ability to synthesize secondary metabolites (SM) in plant tissues [7]. Secondary metabolites, such as phenols, stilbenes, flavonoids and tannins are the major class of inducible protection compounds in many woody species and SM accumulate in forest tree tissues [8]. Austrian scientists recently found that SM increment in spruces was significantly related to the tree ability to recognise pathogenic fungus C. rhododendri, since the tree can increase its SM content when the plant detects risk of biotic stressors [9]. Genetic resources of forest trees are hereditary, accordingly, better genetic trees can have an actual or potential value for economy, environment and science [10]. Previous studies [11-13] have shown that different tree genotypes can synthesize different levels of SM, what can lead to large changes in the diversity of plant microbiota. Therefore, tree genetic selection is purposeful and important factor in maintaining and enhancing forest biodiversity.

The research object – the most widely distributed tree species in Lithuanian forest: Scots pine (*Pinus sylvestris* L.), silver birch (*Betula pendula* L.) and Norway spruce (*Picea abies* (L.) H. Karst.). According to Lithuanian State Forest Service (2019), Scot pine constitutes approximately 34.5% of the Lithuanian forest area [14] and it is the most widely distributed species in Lithuanian forests and in the world [14;15]. Silver birch constitutes approximately 22% and Norway spruce approximately 21% of the all Lithuanian forest area [14]. These three both species occupy 3/4 of total forest area in Lithuanian, for this reason they are very important for our country ecosystem development and economy. Biomass of forest trees is an extremely relevant feedstock for industrial production of various biological materials and has large useful properties for management of forest ecosystem [16]. Highly developed forestry Europe countries *Pinus sylvestris*, *Betula pendula* and *Picea abies* seedlings use in reforestation programs, what shows high-tech importance in these species seedlings performance and resistance [17]. Unfortunately, these species are highly sensitive for pathogens and scientists try to find methods, which can help to reduce damage of pests for these forest trees.

Field of the innovative methods and technologies which can help to achieve better plants growth and sustainability in the process of pathogens attacks is up to date. However, analysis of chemical compounds influence on pathogens in tree species are widespread, but still there is a gap in studies related how physical stressors can impact amount of SM in the different tree species. Plants change their physiological or biochemical properties when they get signals which are induced by various stressors. These changes are related to selective modulation of protein expression in the growing seedling. The first confirmation that temperature affects the epigenetic memory and subsequently has a sustained effect throughout the ontogenesis of the plant (derived from the seeds) during zygote embryogenesis and seed maturation, obtained during reasearch with Norway spruce. According to references [18-23], cold plasma (CP) and electromagnetic field (EMF) have potential in high-tech forestry sciences. Moreover, these technologies are eco-friendly, safe and they can activate seed germination but do not cause genetic mutation at the same time [8;24-26]. Plant seed treatment with CP and EMF is recognized as an innovative tool to increase seed germination and promote plant biomass production [24;27]. In addition, Lithuanian scientists found that seed treatment with CP and EMF causes specific changes in seed protein expression and phytohormone content, long-term growth of perennial plants [17;28;29]. It was observed that Norway spruce seedlings growing from CP processed seeds had significantly more trichomes (needle structures accumulating SM), what implies that seedlings can synthesize more SM, which are responsible for tree itself protection against pests. The common studies are done in agriculture field, where the experiments performed with tomato, pea, cucumber, salad and wheat seeds treatment with CP and EMF had higher germination percent, increased number of leaves per plant and yield, compared to control [25;30-36]. Studies showed that seed treatment with CP and EMF increased total phenolic content (TPC), compared to control in the *Echinacea purpurea* and *S*. bachtiarica leaves [28;37]. In addition, exposure of CP and EMF can increase TPC and reduce germination time of perennial plants (e.g., Norway spruce, Smirnov's rhododendron, Black mulberry) [17;29]. Furthermore, there is identified that seed treatment with EMF had significant positive effects on shoot length, plant biomass and seedling dry mass [35;38]. Plant antioxidant activity is very important for food, medicine and cosmetic industry. As same as TPC, plants can increase their antioxidant activity and concentration of photosynthesis pigments when seed are induced with CP [24;25;27;28;39]. Physical stressors exposure on seeds cause changes of plant phenology, one of the main attributes for plants adaptation to frost and climatic conditions. Cold plasma and electromagnetic field for seed treatment is a new pattern in woody plants research and complex mechanisms of interactions are not fully understood, however, it holds great promises for the future perspectives [27].

The main purpose of our research is to improve the quality and resistance of the Lithuanian main forest tree species – Scots pine, Norway spruce and Silver birch, using a combination of innovative genetic and physical methods. It is important to select particular tree genotypes, potentially more resistant against pathogenic microorganisms and to enhance their resistance of diseases, using seed treatment with physical stressors. This particular pattern would be beneficial as a tool for reforestation management. Selected and processed seeds could be recommended in order to effectively activate plant growth, to increase forest productivity and to reduce pathogenic damage in the future.

Keywords: genetic families, physical stressors, needles, Norway spruce, Scots pine, Silver birch, pathogens

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# FUNCTIONAL DIVERSITY OF MICROBIAL COMMUNITIES IN SCOTS PINE (PINUS SYLVESTRIS L.) AND NORWAY SPRUCE (PICEA ABIES (L.) KARST.) FORESTS

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#### ABSTRACT

Scots pine (*Pinus sylvestris* L.) and Norway spruce (*Picea abies* (L.) H. Karst.) are of the most common conifers on earth. Unfortunately, conifer forests are under threat in many parts of the world. Microbial communities are the unseen biomass largely responsible for the functioning of forest ecosystems. However, beyond the well-known mycorrhizal associations, little is known about the diversity or function of the communities of fungi associated with conifer needles or the considerable diversity of other soil and root-associated microbes. **The aim** of the present study was to comprehensively study the diversity of fungal species associated with Scots pine and Norway spruce needles and their functioning in different environmental conditions. Sampling of needles, was carried out during April – August 2019, in the forests stands in Lithuania. In each research plot the health status, the damage category, the nature of the damage, visual assessment of tree crown defoliation, dechromation and dry branch content in the crown of 30 trees per plot were determined.

DNA was isolated separately from samples of pine and spruce, a DNA fragment of the ITS2 rRNA gene region of each sample was individually amplified and subjected to high-throughput sequencing. Results are expected to reveal the overall diversity of microorganism in needles of Scots pine and Norway spruce demonstrate differences on fungal functional diversity, which strongly influence the health of the stands.

Keywords: Fungi, Biodiversity, Conifer, Functional diversity

#### INTRODUCTION

There is growing recognition among the scientific community and policy makers that sustainable forest management is affected by multiple factors associated with global change (Dávalos and Morosini, 2000; Buchy and Hovermanm, 2000; Mbairamadji, 2009; Ramsfield *et all.*, 2016; Martínez-Falero *et al.*,2017). A changing climate may worsen many of the threats to forests, such as pest outbreaks, fires, human development, and drought. These disturbances can reduce forest productivity and change the distribution of tree species (Spiecker, 2003; Lafleur et al., 2010; Evans & Brown, 2017). However, it is well known that beneficial plant-associated microorganisms may stimulate plant growth and enhance resistance to disease and abiotic stresses (van der Heijden, Bardgett & van Straalen 2008; Baldrian, 2017; Uroz et al., 2016). Microorganisms make a significant contribution to the metabolism, ecology and evolution of trees (Gimenez *et al.*, 2007; Aly, Debbab and Proksch, 2011). Studies of the ecological and evolutionary relationships between plants and their associated microbes have long been focused on single microbes, or single microbial guilds, but in reality, plants associate with a diverse array of microbes from a varied set of guilds.

Scots pine (*Pinus sylvestris* L.) and Norway spruce (*Picea abies* (L.) H. Karst) are the most abundant conifers on Earth (Matías and Jump, 2012). In Europe, pine plantations exceed 28

million hectares, which is more than 20% of the productive forest area, from Spain in the west to the far east of Russia (Durrant, de Rigo and Caudullo, 2016). Norway spruce climate is the main type of conifers of temperate and subalpine forests, Central (in the mountains) to Northern and Eastern Europe and to the Ural Mountains (Chodak *et al.*, 2015).

Coniferous plants interact with a suite of microorganisms representing a variety of ecological functions and lifestyles including mutualistic mycorrhizal fungi (Smith and Read, 2008), pathogenic eukaryotic microbes (Fogel, 1988), and foliar bacterial and fungal endophytes (Carroll, 1988; Pirttilä et al., 2005; Arnold et al., 2007; Carrell and Frank, 2014, 2015; Oono et al., 2014). Foliar pathogens infect and cause disease that is limited to the needles, but can, at high infection levels, cause growth reductions as a consequence of reduced photosynthetic capacity (Hanso & Drenkhan, 2012; Manter et al., 2003; Van der Pas, 1981). Needle diseases cause tree mortality only in the most severe cases. However, the relationships between conifers and their microbes may be particularly important since conifers grow in impoverished acidic soils at both mid and high latitudes, potentially facilitated by their relationship with various microbes (Axelrod, 1986; Lepage et al., 1997; Richardson, 2000; Carrell and Frank, 2014).

Several factors influence the foliar fungal community composition, such as host, nutrient content of the needles, needle age, temperature, precipitation, and pollution (Helander, 1995; Hoffman and Arnold, 2008; Larkin et al. 2012; Zimmerman and Vitousek, 2012). The aim of this study was to assess the diversity and composition of fungal communities in living needles of *Pinus sylvestris* and *Picea abies*. Needles were sampled across the natural distribution range of both conifers in Lithuania, including sites under different environmental conditions. This was expected to demonstrate potential site-specific effects of environmental conditions on fungal biodiversity, community composition and function of microbial communities.

#### METHODOLOGY

#### Site description and sampling

Sampling in Lithuania was conducted during April-May 2019. Needle samples were collected in 30 research plots in a premature Norway spruce and in 30 premature Scots pine stands (based on the forest inventory data) evenly distributed throughout the territory of Lithuania (Figure 1). Research plots of the same species were set along  $\geq 16$  km distance from each other. The study sites were chosen to be as close as possible to the typical pine and spruce habitats.



Fig 9. Map showing locations of 30 Norway spruce and 30 Scots pine research sites in Lithuania

In each research plot the health status (sanitary condition), the damage category (Воронцов *et al.*, 1991), the nature of the damage (mechanical, insect, disease, abiotic factors), visual assessment of tree crown defoliation (%), dechromation (%) and dry branch content in the crown (%) (Ozolinčius & Stankenas, 1996) of 30 trees per plot were determined. A total of 900 spruce and 900 pine trees were assessed.

Sampling of previous year needles were conducted from the upper third of the crown, with 2 replications from 10 trees per research plot. A total of 40 (10 trees x 2 rep. = 20 samples per species) needles samples from both Norway spruce and Scots pine trees in research plots were collected.

#### Molecular identification of fungal communities

In the laboratory field samples were freeze-dried at - 60°C for 24 h. After freeze drying individual samples will be initially ground with the 'Laarmann LAB WIZZ' grinding machine, then 50 mg of each sample will placed into separate 2.0-ml microcentrifuge tubes.

Fungal DNA from the homogenized material were extracted using the standard CTAB protocol (Rosling et al. 2003). Within the same study site, samples were pooled altogether resulting in 30 DNA samples from the needles.

Amplification by PCR of the ITS2 rRNA region was done using barcoded fungal specific primer gITS7 (Ihrmark et al., 2012) and barcoded universal primer ITS4 (White et al., 1990). PCR was performed in 50  $\mu$ L reactions containing 4  $\mu$ L of DNA template. Each reaction included 1% of DreamTaq Green Polymerase (5  $\mu/\mu$ L) (Thermo Scientific, Waltham, MA, USA); 11% of 10× Buffer; 11% of dNTPs (10 mM); 1% of MgCl2 (25 mM); 2% of each primer (200 nM) and 71% of milli-Q water. Amplifications were performed using the Applied Biosystems 2720 thermal cycler (Foster City, CA, USA). The PCR products were analyzed using gel electrophoresis on 1% agarose gels stained with Nancy-520 (Sigma-Aldrich, Stockholm, Sweden). PCR products were purified by centrifugation in 1:20 volume of 3 M sodium acetate (pH 5.2) (Applichem Gmbh, Darmstadt, Germany) and 96% ethanol mixture. Purified PCR products were quantified using a Qubit fluorometer 4.0 (Thermo Fisher

Scientific, Waltham, MA, USA), and an equimolar mix of all PCR products were used for high-throughput sequencing using Pacific Biosciences platform (Menlo Park, CA, USA). Construction of the sequencing library and sequencing using Sequel II one SMRT cell was done at the SciLifeLab (Uppsala, Sweden).

#### **Bioinformatics and Statistical Analyses**

The sequences generated were subjected to quality control and clustering in the SCATA NGS sequencing pipeline (http://scata.mykopat.slu.se). Quality filtering of the sequences included the removal of short sequences (<200 bp), sequences with low read quality, primer dimers and homopolymers, which will collapse to 3 base pairs (bp) before clustering. Sequences that were missing a tag or primer will be excluded. The primer and sample tags was removed from the sequence, but information on the sequence association with the sample were stored as meta-data. The sequences was clustered into different taxa using single-linkage clustering based on 98% similarity. The most common genotype (real read) for each cluster were used to represent each taxon. For clusters containing only two sequences, a consensus sequence was produced. Fungal taxa were taxonomically identified using both the RDP classifier available at https://pyro.cme.msu.edu/index.jsp (Centre for Microbial Ecology, Michigan State University, Michigan, USA) and GenBank (NCBI) database using the Blastn algorithm. The criteria for identification were: sequence coverage >80%; similarity to taxon level 98–100%, similarity to genus level 94–97%. Sequences not matching these criteria were considered unidentified and will be given unique names

Shannon index characterizing the diversity and composition of fungal communities was calculated using R software (Oksanen et all., 2019).

## RESULTS

The presented results are part of an extensive research and reflect only an incomplete part of the overall study results.

Amplification of fungal ITS2 rDNA from all needle samples, PacBio sequencing and quality filtering resulted in 125,567 high quality reads.

Pinus sylvestris				Picea abies					
Sample plot	Forestry	No.of Seqences	No.of FT*	SDI **	Sample plot	Forestry	No.of Seqences	No.of FT*	SDI **
1P	Anykščių	4221	65	0.34	1E	Anykščių	1632	139	3.37
2P	Druskininkų	2715	134	3.14	2E	Jonavos	1938	186	4.1
3P	Druskininkų	947	64	2.97	3E	K. Rūdos	5283	302	4.27
4P	Druskininkų	791	89	3.15	4E	K. Rūdos	4201	112	3.48
5P	Jonavos	2532	26	0.14	5E	Kretingos	481	77	3.36
6P	Jonavos	2183	175	3.63	6E	Kretingos	676	51	1.24
7P	K. Rūdos	2015	184	4.13	7E	Kupiškio	876	153	4.34
8P	K. Rūdos	2031	171	3.21	8E	Kupiškio	1104	139	3.88
9P	K. Rūdos	2547	181	3.84	9E	Mažeikių	738	105	3.34
10P	Kretingos	3197	236	4.31	10E	Nemenčinės	253	85	3.79
11P	Kretingos	2221	95	1.14	11E	Pakruojo	1018	132	3.52
12P	Kupiškio	720	99	2.73	12E	Pakruojo	2738	215	3.81

Table 1. The diversity and distribution of fungal taxa sequenced from needles of *Pinus sylvestris* and *Picea abies*.

13P	Kuršėnų	3710	176	3.09	13E	Panevėžio	3170	203	4.23
14P	Mažeikių	35	21	2.89	14E	Prienų	4320	230	3.93
15P	Nemenčinės	772	138	4.12	15E	Raseinių	4146	232	3.86
16P	Raseinių	3915	210	3.96	16E	Rietavo	3113	176	3.35
17P	Rietavo	938	154	4.26	17E	Rokiškio	5314	197	3.44
18P	Rokiškio	5694	85	0.96	18E	Šakių	3457	151	3.41
19P	Šakių	7357	309	4.29	19E	Šalčininkų	1173	170	4.15
20P	Šalčininkų	2435	238	4.35	20E	Šiaulių	2961	189	3.28
21P	Švenčionėlių	1308	155	4.06	21E	Švenčionėlių	4652	211	3.77
22P	Tauragės	5845	113	0.81	22E	Tauragės	2190	150	3.1
23P	Telšių	1546	167	4.21	23E	Telšių	3238	202	4.11
24P	Trakų	906	131	3.94	24E	Telšių	3260	209	4.26
25P	Ukmergės	403	89	3.68	25E	Trakų	2672	150	3.49
26P	Ukmergės	1346	168	4.08	26E	Ukmergės	740	91	3.32
27P	Utenos	55	17	1.98	27E	Ukmergės	427	76	3.15
28P	Valkininkų	258	68	3.23	28E	Utenos	1124	119	3.22
29P	Valkininkų	428	108	3.96	29E	Valkininkų	777	95	3.58
30P	Veisiejų	276	50	2.88	30E	Valkininkų	780	102	3.53

\* No.of FT: numbers of Fungal taxa; \*\* SDI: Shanon diversity index

Sequence assembly and BLASTn analyses showed that the fungal community in the needles was composed of 1710 fungal taxa (Table 2). Nonfungal taxa and singletons were excluded. The detected fungi in Pine needles were 87.3% Ascomycota, 11.2% Basidiomycota, 1.1% Glomeromycota, 0.2% Chytridiomysota and Zygomycota, respectively. Fungal community in Spruce needles consisted of 81.8% Ascomycota, 17.2% Basidiomycota, 0.5% Glomeromycota, 0.3% Zygomycota, 0.2 % Chytridiomysota.

Table 2. Relative abundance of the 20 most common fungal taxa sequenced from needles of *Pinus sylvestris* and *Picea abies*.

-	Phylum*	Species	GenBank Reference	Compared (bp)	Similarity (%)	Total (%)
	А.	Dothideomycetes sp. 4720_5	KX908472.1	236/238	99	13%
	A.	Cladophialophora sp. 4720_4	FJ008678.1	255/255	100	4%
	А.	Phacidium lacerum	MN588163.1	239/239	100	4%
	A.	Rhizosphaera kalkhoffii	MN547387.1	256/256	100	3%
SI.	A.	Chaetothyriales sp.4720_1	JQ342183.1	256/258	99	3%
estr	А.	Archaeorhizomyces sp. 4720_0	JN006470.1	207/207	100	2%
$V_{V}$	A.	Microsphaeropsis olivacea	MT561396.1	249/249	100	2%
S	A.	Hypoxylon sp 4720_10	MT735206.1	334/345	98	2%
sп	A.	Cladosporium herbarum	MT635288.1L	243/243	100	2%
in	В.	Coleosporium senecionis	MK697293.1	322/322	100	2%
<b>d</b>	А.	Cladophialophora sp. 4720_27	AM902002.1	262/262	100	2%
	В.	Trichosporon sp. 4720_21	AM902002.1	308/308	100	2%
	A.	Lecanora sp. 4720_19	MN902396.1	247/247	100	1%
	A.	Phaeosphaeria marciensis	MH862003.1	248/250	99	1%
	А.	Phyllosticta sp. 4720_49	MN902356.1	259/259	100	1%
	A.	Cyphellophora sessilis	NR_132823.1	293/297	99	1%

	A.	Phaeococcomyces eucalypti	NR_120226.2	246/248	99	1%
	A.	Trichomerium sp. 4720_23	LR865156.1	260/266	98	1%
	A.	Helotiales sp. 4720_25	KY742593.1	242/242	100	1%
	B.	Malassezia restricta	LT854697.1	369/369	100	1%
	Total of 20	taxa				51%
	А.	Aspergillus pseudoglaucus	HQ873371.1	259/259	100	29%
	А.	Dothideomycetes sp. 4720_5	KX908472.1	236/238	99	8%
	А.	Rhizosphaera kalkhoffii	MN547387.1	256/256	100	3%
	A.	Chaetothyriales sp.4720_1	JQ342183.1	256/258	99	2%
	A.	Trichomerium sp. 4720_23	LR865156.1	260/266	98	2%
	A.	Cyphellophora sessilis	MH860834.1	280/280	100	2%
	A.	Cladophialophora sp. 4720_4	FJ008678.1	255/255	100	2%
S	A.	Archaeorhizomyces sp. 4720_0	JN006470.1	207/207	100	1%
bie	А.	Phacidium lacerum	MN588163.1	239/239	100	1%
al	А.	Hypoxylon sp 4720_10	MT735206.1	334/345	98	1%
ы	A.	Chaetothyriales sp. 4720_15	KJ827089.1	264/269	98	1%
ic	B.	Lactarius sp. 4720_8	KP887932.1	319/337	95	1%
D	A.	Cladophialophora sp. 4720_27	AM902002.1	262/262	100	1%
	G.	Acaulospora sp. 4720_14	KM494484.1	290/290	100	1%
	А.	Unidentified sp. 4720_61	MN902480.1	284/284	100	1%
	A.	Microsphaeropsis olivacea	MT561396.1	249/249	100	1%
	B.	Malassezia restricta	LT854697.1	369/369	100	1%
	A.	Chaetothyriales sp. 4720_12	KP400572.1	256/256	100	1%
	A.	Exophiala sp 4720_79	KF823617.1	277/292	95	1%
-	Total of 20	taxa				60%

\*A - Ascomycetes, B - Basidiomycetes, G - Glomeromycetes

Information on the 20 most common fungi taxa, which represent 62% of the fungi diversity found in Scots pine and 46% in Norway spruce is relative to all fungi sequences in each dataset. The most common fungi found in the needles of Scots pine were *Aspergillus pseudoglaucu* (23% of all fungal sequences), *Dothideomycetes* sp. 4720\_5 (7%), *Eurotiomycetes* sp 4720\_1 (3%), *Rhizosphaera kalkhoffii* (3%) (Table 2). The most common fungi in the needles of Norway spruce were *Teratosphaeria* sp. 4720\_5 (13%) of all fungi sequences, *Cladophialophora* sp. 4720\_1 (4%), *Phacidium lacerum* (4%) and *Rhizosphaera kalkhoffii* (4%) (Table 2). In general, the dominant fungal community in the needles of Norway sprucebelonged to the class Dothideomycetes, meanwhile, in the needles of Scots Pine to the Eurotiomycetes (Fig. 4).

The Shannon diversity indexes in pine and spruce stands were between 0.34–4.35 and 1.24–4.34, respectively (Table 1).



Fig. 4 The relative abundance of different fungal classes in living needles from *Pinus sylvestris* and *Picea abies* 

## DISCUSSION

These studies investigated the functional biodiversity of fungi in the needles of Scots pine and Norway spruce under different environmental conditions in Lithuania. Although previous studies have identified Leothiomycetes as one of the most common classes of fungi associated with pine needles (Ganley and Newcombe, 2006; Terhonen et al., 2011), in our study, this class was only fourth in frequency. In contrast to the previous studies, our results showed that pine needles were mainly colonized by fungi of the class Eurotiomycetes. These differences may have been due to incomplete amount of information, as it's only a part of data which was analised, on the other hand, this trend could be a response to external (or internal) factors stressing the plant.

Among the most common species of fungi on *P. sylvestris*, five phytopathogens and five endophytes were found, some of which, in one way or another, manifest themselves as saprotrophs. Class Eurotiomycetes it is a huge class of fungi, among which there are toxinproducing fungi, saprotrophs and plant endophytes (Geiser *et al.*, 2017). These fungi are widespread throughout the world and are often described as endophytes of conifers, for example: *Alternaria* spp., *Pestalotiopsis* spp., *Preussia* spp., and others (Jeewon *et al.*,2018; Quardi *et al.*,2014). Usually they are not direct pathogens, but they are often found on the affected tissues as hemibiotrophs and saprtrophs. Nevertheless, the variety of these fungi is huge, and there is lack of information about the representatives of this class, except for the occurrence. *Phacidium lacerum* discovered by us is a dangerous plant pathogen, a quarantine species that acts not only as a pathogen, but also as a saprotroph, colonizing already dead plant tissues (Roll-Hansen, 1989; Matías and Jump, 2012; Ozturk and Amiri, 2020). In the Global Biodiversity Information Facility (GBIF) database, the findings of this pathogen on Scots pine in Serbia, Norway, Estonia, Switzerland, Denmark and other countries were previously noted (Registry-Migration.Gbif.Org, 2019). In addition, it affects not only Scots pine, but also Norway spruce, pseudotsuga and other plants, including fruit crops (Roll-Hansen, 1989). *Phacidium lacerum* is often found as an endophyte in pine needles, but this does not mean that under unfavorable environmental conditions this fungus will not become a phytopathogen, causing snow/needle blight (Tanney and Keith, 2018).

*Rhizosphaera kalkhoffii* Bubák, is also representative species of the Dothiodeomycetes classe. *R. kalkhofii* is a phytopathogen fungy which provocate needle blight (CABI). The life cycle of this fungus allows it to survive both in fallen needles, where it is more often found, and in living, as an endophyte. (You *et al.*, 2013; Millberg, Boberg and Stenlid, 2015; Nguyen *et al.*, 2016). Often, the symptoms of this disease remain invisible, most often the lower branches are affected first. (Juzwik, 1993). This fungi is ubiquitous in Europe and causes significant damage (Belomesyaceva and Fedorov, 2008). Previously, in Lithuania, it was quite rare, however, this fungus can cause significant damage to *P.sylvestris* (Treigine, 1998). Despite the fact that the fungus brings more harm in more northern latitudes, such as in Norway, additional research is required in Lithuania to study how strongly this fungus affects the health of *P.sylvestris* (Belomesyaceva and Fedorov, 2008).

*Coleosporium senecionis* Boerema & Verh. is a phytopathogen causing needle rust, and it is found in Europe, Asia and America (Registry-Migration.Gbif.Org, 2019). Infections leading to the death of the entire tree are rare, but subsequent infections accompanied by additional stress, such as drought, can result in loss of vitality, loss of growth, and death of the entire tree (nrcan.gc.ca). Trees that are less vigorous are more susceptible to attacks from other insects and diseases such as the bark beetle *Ips* sp. or root rot *Armillaria ostoyae* (Romagn.) Herink (nrcan.gc.ca).

*Microsphaeropsis olivacea* (Bonord.) and *Cladosporium herbarum* (Pers.) Link, was previously noted as an endophyte of Scots pine needles (Lazarević and Menkis, 2020; Wang and Guo, 2007; Zamora, Martínez-Ruiz and Diez, 2008). Interestingly, Ganley and Newcomb (2006) noted that Lophodermium species were absent with higher occurrences of Hormonema and Cladosporium, suggesting that these species may have some antagonistic effect on Lophodermium species, which are commonly found in the needles of conifers (Terhonen *et al.*, 2011).

Most common spicies of fungi on Norway spruce were phytopathogens, endophytes and saprotrophs. Class Dothiodeomycetes contain a large number of phytopathogens, including patogens of spruce needles, such as: *Dothistroma septosporum* (Dorog.) M. Morelet, *Rhizosphaera kalkhoffii*(RIZSKA), *Lecanosticta acicola* (Thüm.), *Septorioides strobi* Wyka & Broders etc. *Dothistroma septosporum* is the causal agent of red-band needle blight. This necrotrophic pathogen causes red streaks on infected needles and kills them (Jankovský, Bednářová and Palovčíková 2004). *Dothistroma septosporum* is also widespread in Lithuania (Markovskaja and Treigienė 2009). *Lecanosticta acicola* on *P. sylvestris* is known as brown spot needle blight (van der Nest *et al.*, 2019). Many of the representatives of this class are not strictly species-specific, and also previously gravitated towards warmer regions. Contrary, now we can see how rapidly they are expanding to northern regions, which was also confirmed by our research (van der Nest et al., 2019).

*Rhizosphaera kalkhoffii* Bubák is a harmful phytopathogenic fungus. This fungus is found in live and fallen needles (Livsey and Barklund, 1992). It is especially dangerous in places where drought can occur (Murray, 1957; Diamandis, 1978). *Phacidium lacerum* is found as

endophyte in the needles of other spruce species such as *Picea rubens*. The species is also associated with diseases of *Pyrus* and *Vaccinium* fruit rot after harvesing, and known as endophyte, saprotroph and pathogen of conifers (Tanney and Seifert, 2018). This saprotrophic and opportunistic fungus can asymptomatically infect host tissue until optimal conditions for extensive colonization and reproduction arise (Tanney and Seifert, 2018; Sieber, 2019). Also *P. lacerum* is capable of persisting in coniferous litter, which may increase its transmission (Asplund *et al.*, 2019).

*Microsphaeropsis olivacea* (Bonord.) Höhn., *Malassezia restricta*, *Aspergillus pseudoglaucus* in the literature is noted as endophytes inhabiting the needles of coniferous trees (Persson, no date; Lorenzi, Lorando and Picco, 2006; Wang and Guo, 2007; Bußkamp, Langer and Langer, 2020). *Aspergillus pseudoglaucus* Blochwitz (1929) is also xerophilic and has not previously been reported as an endophyte in conifers (Visagie *et al.*, 2017). This is rather uncommon, but perhaps this is due to the fact that most studies of endophyte communities are based on pure cultures isolated in artificial environments, and it is difficult to determine the degree of representativeness of their results for natural infections in terms of the number and occurrence of species (Qadri et al., 2014). Both endophytes that asymtomaticly affect plants, and potential dangerous phytopathogenic fungi under favorable conditions are capable of provoking a disease of Scotch Pine and Norway spruce needles. The examination of endophytes in asymptomatic external needles can help prevent the development of a future disease in a timely manner.

## CONCLUSIONS

Our preliminary results clearly demonstrate differences on fungal communities detected from Norway spruce and Scots pine needles, which were not dependent on environmental conditions. However, these findings should not be considered as final and reliable, because an incomplete data set could severely skew the results.

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# ENDOPHYTIC BACILLUS SPP. STIMULATE TOBACCO (NICOTIANA TABACUM L.) SHOOT GROWTH UNDER IN VITRO CONDITIONS

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#### EXTENDED ABSTRACT

#### **OVERVIEW**

Plant propagation *in vitro* techniques based on axillary bud proliferation find application in plant biology research, germplasm preservation and industrial-scale production of vegetatively propagated plants [1,2]. *In vitro* environment constitutes a set of conditions, such as the composition of cultivation media, low irradiance, low CO<sub>2</sub> concentration during the light period, high air humidity. These variables could lead to the imbalance of plant physiological equilibrium and stress [3-6], resulting in slow plant growth, early senescence or severe physiological responses, such as habituation or hyperhydricity [7,8].

Plants are closely associated with the group of endosymbiotic microorganisms that live in plant tissues such as bacteria and fungi [9,10]. Plant growth-promoting properties of endophytes have been extensively studied (see recent reviews by [11-13]). Often *in vitro* plant cultures have been considered axenic, therefore, the composition and role of the endophytic microbiome of *in vitro* plant tissues attracted little attention and the occurrence of bacterial growth in tissue cultures has been regarded as contamination resulting from endophytic bacteria overgrowth [14-18]. However, several studies have also shown that endophytic bacteria are common in plant tissues grown *in vitro* [10,16,19] and their composition depends on explant origin and cultivation conditions. During the last decade, beneficial effect on plant growth, acclimatization or rooting was demonstrated for endophytic bacteria isolated from *in vitro* cultures of strawberry [20], grapevine [21], tomato [22] and sweet cherry [23].

Engineering of the endophytic microbiome of *in vitro* plant tissues has the potential to improve their acclimation to stress induced by the *in vitro* conditions [9]. Therefore, the aim of this study was to identify *Nicotiana tabacum* endophytic bacteria isolates capable to promote biomass accumulation of *in vitro* shoots. We isolated culturable endophytic bacteria from leaves of greenhouse-grown cultivated tobacco plants and assessed their capability to colonise tissues of tobacco shoot culture *in vitro* and to promote biomass accumulation of the shoots.

A diversity of *N. tabacum* endophytic microbiome was assessed using cultivation and 16S rRNA gene analysis methods. Forty-nine endophytic bacteria isolates were obtained from greenhouse-grown tobacco plant shoots and were identified as *Bacillus* sp. and *Pseudomonas* sp. Twenty-one of the isolates were used to study endophytic bacteria effect on tobacco shoot growth *in vitro*. The shoots were inoculated with bacterial suspension and shoot fresh weight was assessed after 3 weeks of cultivation. Isolates of *B. wiedmannii* Nt.3.2, *B. mycoides* Nt10.1, *B. toyonensis* Nt.18, Nt.20.2 promoted shoot growth 11 % to 21 %. Interestingly, FW of shoots inoculated with isolates of the same species, such as *B. wiedmannii* Nt.14.2, *B. mycoides* Nt.25, Nt.12.1, and *B. toyonensis* N.37, was reduced 5 % to 11 % or the bacteria had no significant effect on shoot growth. Inoculation with the remaining isolates of *B. aryabhattai*, *B. marisflavi*, and *B. simplex* had no significant effect on biomass accumulation or was detrimental to tobacco shoot growth. The results suggest that isolates with a contrasting effect on shoot growth represent the capability of multiple bacterial strains to establish different interactions with the host. The isolates of *Bacillus* sp. with shoot growth-promoting properties have a potential application to improve the growth of plant tissue culture *in vitro*, and further studies based on their interaction with plant and host specificity would aid practical implementation.

#### METHODS

Seeds of cultivated tobacco (*Nicotiana tabacum* L.) were planted on non-sterile or autoclaved peat substrate in plastic pots ( $10 \times 10 \text{ cm}$ ) and grown under greenhouse conditions for one week after seedling emergence. Fresh tobacco leaves were surface sterilized using a modified protocol described by Zhang, et al. [24]. The leaves were thoroughly washed with running tap water, rinsed with 70 % ethanol and

incubated for 4-5 min in 2.5 % sodium hypochlorite. Subsequently, the samples were washed for 30 s with 75 % ethanol and rinsed three times with sterile deionized water. The water from the final rinse was plated out on lysogeny broth (LB) agar [25] to confirm that the surface sterilization process was successful. The leave tissues were mechanically homogenized in sterile deionized water and plated on LB medium. Plates were incubated at 25 °C for 2 to 5 days depending on bacterial colony growth. The bacteria isolates were selected based on distinct colony morphology and further purified by repeated streaking on LB agar. Isolates were grown in LB broth, the medium was supplemented with 25 % (v/v) glycerol and stored at -70 °C.

Bacterial DNA was isolated using the GeneJET Genomic DNA Purification kit (Thermo Fisher Scientific Baltics, Lithuania). The 16S rRNA gene sequence was amplified using the universal primers E8F (5' AGAGTTTGATCCTGGCTCAG 3') and E1541R (5' AAGGAGGTGATCCAGCC 3') [26]. PCR was conducted using 0.5 µM primer, and MyTaqTM Mix 2X (BioLine) under the following conditions: pre-denaturation (94 °C, 2 min), denaturation (94 °C, 30 s), annealing (55 °C, 45 s), and elongation (72 °C, 2 min) for a total of 40 cycles, followed by a final elongation (72 °C, 10 min). PCR products were purified using the GeneJET PCR Purification kit (Thermo Fisher Scientific Baltics, Lithuania) and sequenced from both ends using the same primers (BaseClear, Netherlands). To reduce bias from sequencing errors, 100 and 20 nucleotides were removed from the beginning and end of the sequences, respectively, and sequences obtained using forward and reverse primers were combined into a single sequence of approx 1400 bp. The 16S ribosomal RNA sequences (Bacteria and Archea) database was queried at the NCBI BLAST server [27] using identity cut of value 98.65 % for species [28] and 95 % for genus [29]. Whole-genome sequence analysis and assembly were performed by BaseClear Ltd. using Illumina paired-end sequencing on the MiSeq system. Taxonomic classification of the genome assemblies was performed using GTDB-Tk v1.1.0 toolkit [30] and the Genome Taxonomy Database (GTDB) release 95 [31].

Shoot culture of cultivated tobacco was maintained on solid Murashige-Skoog (MS) medium [32], supplemented with 0.75 mg l<sup>-1</sup> 6-benzylaminopurine, 30 g l<sup>-1</sup> sucrose and 0.8 % agar in a climatic chamber (SANYO Electric Co., Japan) at 25±3 °C, under fluorescent lamp illumination 150  $\mu$ mol·m<sup>-2</sup>·s<sup>-1</sup> intensity and 16/8 h light/dark photoperiod. After four weeks of cultivation, the shoots were transferred to a fresh medium and were used for bacterial inoculation the next day. Uninoculated plants were used as a control.

Shoot inoculation experiments were carried out as described previously by Tamošiūnė, et al. [33]. Bacterial inoculum initiated from a glycerol stock was grown in LB broth at 25 °C to an exponential growth phase. Bacteria were sedimented by centrifugation and resuspended in MS medium at a concentration of  $\sim 10^7$  CFU/ml. Three microliters of the bacterial suspension were inoculated on several nodes of shoot petiole. MS medium without bacteria was used for the control treatment. The inoculated shoots were maintained as described above and shoot fresh weight (FW) was assessed after 3 weeks of co-cultivation. The shoot and endophytic bacteria co-cultivation experiments were carried out two to four times and means of FW was estimated using from 30 to 120 shoot samples. Data are presented as the mean of at least 3 independent experiments and standard error of the mean.

#### RESULTS

Forty-five endophytic bacteria isolates with distinct colony morphology were obtained from fresh leaves of tobacco grown in a greenhouse on peat substrate for one week. Based on 16S rRNA gene sequencing analysis 45 isolates were assigned to six distinct phylogenetic clades including *Bacillus cereus group*, *B. marisflavi*, *B. aryabhattai*, *B. simplex*, *B. pumilus* and *Pseudomonas koreensis*. Isolates of the *B. cereus* group, also known as *Bacillus cereus sensu lato* (*s.l.*), were assigned to three closely related subclades 1A-C. The *B. cereus s.l.* taxonomic group is a subdivision of the genus *Bacillus* that are highly closely related species with conserved genomes (5.2-to 5.9-Mb) and have over 97% similarity with the known species of this group (> 99% in 16S rRNA gene sequences) and less than 95% similarity with other species of the genus *Bacillus*.

In our study, the characteristic rhizoidal colonial morphology supported the relation of the subclade 1C to *B. mycoides* which is genetically distantly related to the *B. cereus* group [34]. The subclades 1A and 1B initially were assigned as *B. thuringiensis* and *B. mobilis*, respectively, based on 16S rRNA sequence data. However, low variability of the 16S rRNA gene sequence and similar colonial morphology within the closely related subclades lead to unequivocal identification results and further genome data analysis of the selected isolates revealed a close relationship to strains of *B. toyonensis* and *B. wiedmannii* for the two subclades, respectively. Difficulties in identification of *Bacillus cereus s.l.* strains have also been addressed in previous studies. Carroll et al. [35] have emphasized the difficulty in reliably

differentiate strains of *B. mobilis* and *B. wiedmannii* which produced overlapping genomospecies in which genomes could share  $\geq$ 95 average nucleotide identity for both species type strains. Using polyphasic analysis of phenotypic and genotypic traits Jimenez et al. [36] clustered *Bacillus* strain MC28 to the *B. toyonensis* group, previously described as *B. thuringiensis*.

Twenty-two of the isolates representing distinct taxonomic groups were used to study endophytic bacteria effect on tobacco shoot growth *in vitro*. The shoots were inoculated with bacterial suspension and shoot fresh weight (FW) was assessed after 3 weeks of co-cultivation. Inoculation with the selected isolates of *B. aryabhattai* (Nt.27, Nt.26), *B. marisflavi* (Nt.41), *B. simplex* (Nt.21, Nt.16.1, Nt.53) and *P. koreensis* (Nt. 32) had either no significant effect on biomass accumulation or the shoot growth was reduced. Three of the isolates *B. wiedmannii* Nt.9.1, *B. pumilus* Nt.12.2 and *B, aryabhattai* Nt.54.1 had a detrimental effect on shoot survival.

*B. cereus s.l.* isolates co-cultivation effect on tobacco shoot biomass accumulation results are presented in Figure 1. Among the twelve isolates, four resulted in a  $11\pm2.9\%$  to  $21\pm4.7\%$  increase in shoot biomass accumulation as compared to the control of untreated shoots, and most of the isolates of this group had no significant inhibiting effect on shoot growth.



**Figure 1.** Endophytic *B. cereus s.l.* isolates co-cultivation effect on tobacco shoot biomass accumulation. Data is presented as the mean and standard error of the mean of co-cultivated tobacco shoot fresh weight (FW) normalized to untreated control. The asterisk indicates mean values significantly different compared to control (\* p<0.05; \*\* p<0.01).

Interestingly, co-cultivation with closely related isolates within the *B. cereus l.s.* resulted in contrasting consequences on the shoot growth. *B. weidmannii* Nt.3.2, promoted shoot growth ( $21\pm4.7\%$  FW increase as compared to control), contradictory results were observed for the isolate Nt.14.2 ( $1\pm3.7\%$  FW decrease comparable to control). Similarly, *B. toyonensis* Nt.18 and Nt.20.2 stimulated an increase in shoot biomass 16±2.9% and 13±5.2%, respectively, but a shoot growth-inhibiting trend was observed for Nt.37. Also, among the seven *B. mycoides* isolates included in the analysis, shoot growth-promoting properties were observed only for Nt.10.1 ( $11\pm2.9\%$  FW increase).

The results suggest that isolates with a contrasting effect on shoot growth represent the capability of multiple bacterial strains to establish different interactions with the host.

#### CONCLUSIONS

Our study showed that isolates of endophytic bacteria of *B. cereus* group isolated from cultivated tobacco leaves can promote tobacco shoot biomass accumulation under *in vitro* conditions. Different shoot growth-regulating properties were observed for closely related isolates of the same species, suggesting that the plant growth-promoting effect is strain specific. The application of isolates provides new opportunities for exploring their potential application to improve the growth of plant tissue culture *in vitro*. Further studies based on their interaction with plant and host specificity would aid practical implementation.

Keywords: Bacillus sp.; endophytic bacteria; microbiome engineering; plant stress

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## PHYTOCOMPOUNDS IN AQUEOUS EXTRACTS: QUALITATIVE SCREENING AND QUANTITATIVE DETERMINATIONS

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#### ABSTRACT

Plants are packed with vitamins and nutrients that are essential to a good human health and act as adjuvants in various illnesses. Some examples of well – known phytochemicals are flavonoids, phenolic acids, isoflavones, isothiocyanates, saponins, carotenoids. Phytochemicals have an important biological role in plants and contribute to their growth and defence against known pathogens. This research paper describes the qualitative screening of phytochemicals and quantitative determinations of different phytocompounds from plants known for their pharmacological benefits to human health: Sea buckthorn, Hyssop, Elderflower, Acacia, Cornflowers, Sorrel, etc. Qualitative screening involves known analytical techniques that are based on the visual change in colour of the aqueous extracts upon adding known chemical reagents.. A quantitative study was carried out in order to determine the total content of flavonoids, total content of terpenoids and total content of polyphenols by recording the UV – Vis spectra at specific wavelengths for each phytocompound. The method used for the determination of total polyphenolic content was the Folin - Ciocalteu (FC) reaction that allows a proper measuring of the reductive ability of an antioxidant.

Keywords: phytocompounds, qualitative screening, quantitative determinations, plants

## **INTRODUCTION**

Phytochemicals are generally described as bioactive nutrient plant compounds found in vegetables, fruits, and other plant – related raw materials that are able to provide appropriate health revenues supplementary to elementary nourishment, therefore helping lower the risk of major chronic illnesses [1]. Some of the phytochemicals capable of boosting human health are polyphenols, flavonoids (simple or phenolic), anthocyanidins, terpenoids, carotenoids, phytosterols, glucosinolates, and fibers. For example, carotenoids, found in abundance in carrots, tomatoes, parsley, spinach, etc., contain antioxidants that may protect against different types of cancer (e.g.: uterine, prostate, lung, digestive) [2].

Plants are rich in a variety of radical scavenging molecules of therapeutic importance, such as alkaloids, amines, vitamins, phenolic acids, terpenoids, etc. that help diminish the damages produced in tissue's structure during physiological transformations [ citation is needed] [3]. The allopathist capacity of plants is a function of their bioactive components that present multiple physiological properties to human health [ citation is needed] [4]. So, the screening of biomolecules permit the detection of compounds that may be used as a base for more modern medicinal drugs that could treat various diseases.

Sea buckthorn (*Hippophae rhamnoides*) contains high amounts of vitamins, fibers, antioxidants and proteins which makes these berries an excellent adjuvant in treating stomach problems, lovering blood pressure and bad cholesterol, boosting immunity and preventing various infections. This orange berry is considered by many a superfruit especially because, with it's one third of size compared to blueberry, contains 12 times the amount of vitamin C as compared to an orange [5]. Hyssop (*Hyssopus officinalis*) is a member of the mint family used since Biblical times for its aromatic properties whose health benefits range from lovering blood sugar, avoid destruction of red blood cells, relieves respiratory issues, enhances digestion, decelerated the growth of various harmful bacteria, etc. [6].

Elderflower (*Sambucus nigra*) is used worldwide in traditional medicine due to its antiseptic and anti-inflammatory characteristics, having also diuretic and laxative properties and research showed that Elderflower has the capacity to kill many hospital germs including methicillin-resistant Staphylococcus aureus (MRSA) [7]. Acacia (*Robinia pseudacacia*) has a long history as a medical ingredient that goes back to ancient Egyptians that used it to treat hemorrhoids. It is used in topical treatments to help wounds heal and researchers believe that this is due to some of its chemical content (e.g.: alkaloids, glycosides, flavonoids, etc) [8].

Cornflowers (*Centaurea cyanus*), an *Asteraceae* family member, is mainly used for cosmetic purposes as a natural remedy for dark circles around the eyes but also acts as an ailment in mucus, tissue and skin inflammation [9]. Sorrel (*Rumex acetosa*) is cultivated worldwide especially for culinary purposes and also has a variety of health benefits: aids in regulating the blood pressure, is an adjuvant in maintaining vision health, prevents anemia (due to its high content in iron), helps boost immunity (a cup of Sorrel leaves contains 106% of the daily vitamin C intake), etc. [10].

Qualitative screening involves different known analytical methods that are based on the change in color of the aqueous extracts prepared from plants once known chemical reagents are added. A quantitative study was carried out in order to determine the total content of flavonoids, total content of terpenoids and total content of polyphenols by recording the UV - Vis's spectra at specific wavelengths for each phytocompound.

This research paper describes the qualitative screening of phytochemicals and quantitative determinations of different phytocompounds from plants known for their pharmacological benefits to human health: Sea buckthorn, Hyssop, Elderflower, Acacia, Cornflowers, Sorrel, etc. Also, to proper evaluate the aqueous extracts, antioxidant activity determinations were carried out using the DPPH (2, 2 - diphenyl - 1 - picrylhydrazyl) method.

#### **MATERIALS AND METHODS**

#### Materials

DPPH (2,2 – diphenyl – 1 – picryl – hydrazyl – hydrate), hydrochloric acid (HCl), sulphuric acid (H<sub>2</sub>SO<sub>4</sub>), copper sulphate (CuSO<sub>4</sub>), copper acetate (Cu(CH<sub>3</sub>COO)<sub>2</sub>), lead acetate (Pb(Ch<sub>3</sub>COO)<sub>2</sub>), catechin standard, gallic acid standard, Folin-Ciocalteu reagent, ferric chloride (FeCl<sub>3</sub>), aluminium chloride (AlCl<sub>3</sub>), vanilin, Millon reagent were purchased from Sigma – Aldricht. Alcohols (e.g.: ethanol - C<sub>2</sub>H<sub>5</sub>OH, methanol CH<sub>3</sub>OH) and sodium hydroxide (NaOH) were purchased from Scharlau. The distilled water was freshly prepared in the laboratory.

## **Preparation of aqueous extracts**

The plants used in our current research study were either purchased already dried as herbal tea (Acacia, Corflowers, Elderflower and Hyssop), dried fruits (Sea buckthorn) or purchased from the local market (Sorrel). In the case of Sorrel, its green leaves were thoroughly washed with tap water and distilled water and dried at room temperature for 10 days away from

sunlight. Aqueous extracts were prepared using the same protocol no matter what plant we've used: 25 grams of dried plant, transferred into a glass beaker and 250 mL double distilled water were added. The resulted mixture was kept in the refrigerator for 24 hours to infuse, then filtered until no solid debris were present in the aqueous extract and stored in the refrigerator in glass flasks for further analyses. All the above-prepared aqueous extracts were stable for up to 12 weeks.

#### Qualitative screening of phytochemicals

Qualitative phytochemical screening use known standard analytical methods that enable the determination of different chemical groups or compounds in the aqueous extracts. These methods rely mainly either on colour or on precipitation reactions as a positive response to the presence of those bioactive compounds giving a hint only about the presence and/or absence of that specific bio-compound and not at all about its amount [11, 12].

#### Qualitative screening for saponins

The general principle involves taking 2 mL aqueous extract and 2 mL distilled water are shaking the resulted solution for 15 minutes in a graduated cylinder. After that, the mixture is left for a couple of seconds and the appearance of a 1 cm foam layer means saponins are present in the analysed aqueous extracts [13].

## Qualitative screening for flavonoids and phenolic flavonoids

The presence of flavonoids is given following the next protocol: 2 mL aqueous extract was mixed with 1 mL 2N NaOH solution. If the resulted solution is yellow and disappears once dilute HCl is added, that is a positive response for flavonoids.

The test for phenolic flavonoids involves mixing 1 mL aqueous extract with 2 mL of 10% lead acetate solution and the formation of a brown precipitate indicates the presence of these bioactive compounds.

## Qualitative screening for proteins and amino acids

Several assays are described in the literature that allow the qualitative evaluation of proteins and aminoacids [14]:

a) Millon test (test for tyrosine): over 1 mL aqueous extract 5-6 drops of Millon reagent are added and, if proteins are present, a white precipitate appears that changes its color to red upon heating.

b) Biuret test: to 3 mL aqueous extract, 3 mL NaOH solution (4%) and couple of drops of 1% CuSO<sub>4</sub> are added; if a purple solution results, than peptide bonds are present in the studied aqueous extracts.

c) Ninhydrin test: this is a general test for aminoacids and the following steps are involved: over 3 mL aqueous extract, 3 drops of 5%  $Pb(CH_3COO)_2$  are added and heated for 10 minutes. A purple or blue colour means that aminoacids are present.

d) Cysteine test: to 5 mL aqueous extract, 2-3 drops of 40% NaOH are added and boiled for 5 minutes. The solution should change either in purple or blue or a black lead sulphate precipitate should form.

e) Xantoprotein test (for tyrosine, tryptophan and phenylalanine): to 3 mL aqueous extract, 1 mL concentrated  $H_2SO_4$  is carefully added. First a white precipitate can be observed that turns yellow after boiling and orange after adding 1 mL NH<sub>4</sub>OH 4%.

## Qualitative screening for alkaloids

Three tests are generally described for alkaloids [15]:

a) Mayer test: to 2 mL aqueous extract, 2 mL of concentrated HCl was added and 2-3 drops drops of Mayer reagent (potassium mercuric iodide). If green solution or a white precipitate appears, than alkaloids ar present.

b) Wagner test: to 3 mL aqueous extract, 1 mL Wagner reagent (iodine in potassium iodide) was added and a reddish-brown precipitate should form.

c) Hager test: to 3 mL aqueous extract, 1 mL Hager reagent (saturated picric acid solution) was added and, if a yellow precipitate is formed, then alkaloids are present.

## Quantitative determinations of different bioactive compounds

The total content of tannins (TCF), flavonoids (TCF) and polyphenols (TCP) involves recording the absorbance at specific wavelenghts for each group of compound, in triplicate (Table 1) [16].

Assay	Reagents	Parameters	Recordings
тст	0.5 mL extract+3 mL 4% vanillin-MeOH and 1.5 mL HCl	15 min.	Absorbance
ICI		incubation	at 500 nm
TCF	1 mL extract+4 mL distilled water and 0.3 mL 5% NaNO <sub>2</sub> ; after 5 min: 0.3 mL 10% AlCl <sub>3</sub> ; after other 5 minutes: 2 mL 1M NaOH and 2.4 mL distilled water	30 min. incubation	Absorbance at 510 nm
ТСР	1 mL diluted extract and 5 mL Folin-Ciocalteu reagent; after 8 minutes: 4 mL Na <sub>2</sub> CO <sub>3</sub>	60 min. incubation	Absorbance at 765 nm

Table 1. Quantitative determinations

## Evaluation of the antioxidant activity using the DPPH assay

The antioxidant activity (AA, %) was evaluated following the 2,2 – diphenyl – 1 – picryl – hydrazyl – hydrate (DPPH) protocol: an ethanoloic solution of DPPH was prepared in and 0.5 mL aqueous extract were mixed with 1 mL 0.02 mg/mL DPPH solution. Then we recorded the absorbance at 517 nm. Also, a blank was prepared: 0.5 mL distilled water were mixed with 1 mL 0.02 mg/mL of the DPPH solution. The antioxidant activity was calculated using the formula below (Equation 1):

$$AA(\%) = \frac{A_{control} - A_{sample}}{A_{sample}} \times 100$$
(1)

where:  $A_{Control}$  represents the absorbance of the blank DPPH and  $A_{Sample}$  is the absorbance of the aqueous extract mixed with 0,02 mg/mL of the DPPH solution.

## **RESULTS AND DISCUSSIONS**

## Qualitative screening for phytochemicals

All the aqueous extracts were prepared using the same protocol, the only difference appeared in the colour of the resulted extracts (Table 2). Aqueous extracts were stable at  $4^0$  C (in the refrigerator) and no visible or morphological alteration occurred for over 12 weeks, highlighting that cold extraction is a viable alternative for obtaining aqueous extracts. The pH

of all the aqueous extracts was measured and the results ranged from 6.5 (Sea buckthorn) to 7.2 (Cornflowers).

Crt. no	Plant	Color
1	Sea buckthorn (Hippophae rhamnoides)	Orange
2	Hyssop (Hyssopus officinalis)	Light violet
3	Elderflower (Sambucus nigra)	Brown
4	Acacia (Robinia pseudacacia)	Light brown
5	Cornflowers (Centaurea cyanus)	Indigo
6	Sorrel (Rumex acetosa)	Light green

Table 2. Colour of the aqueous extracts

## Qualitative screening for saponins

Saponins are plant-derived organic compounds that tend to form a foamy layer once agitated in water [17]. All the studied samples subjected to the qualitative screening for saponins gave a positive response, Acacia showing a maximum of 2.5 cm foam layer and Sorrel having the minimum foam layer of 1.8 cm (Table 3).

Crt. no	Plant	Foam layer
1	Sea buckthorn (Hippophae rhamnoides)	2.3 cm
2	Hyssop (Hyssopus officinalis)	2.3 cm
3	Elderflower (Sambucus nigra)	2.1 cm
4	Acacia (Robinia pseudacacia)	2.3 cm
5	Cornflowers (Centaurea cyanus)	2.5 cm
6	Sorrel (Rumex acetosa)	1.8 cm

Table 3. Qualitative screening for saponins

## Qualitative screening for flavonoids and phenolic flavonoids

Of all the analysed 6 aqueous extracts, the qualitative screening revealed the presence of flavonoids only in 4 samples, namely the flower – derived aqueous extracts: Hyssop, Elderflower, Acacia and Cornflowers. On the other hand, the qualitative evaluation of phenolic flavonoids resulted in their absence in all the studied aqueous extracts.

## Qualitative screening for proteins and amino acids

Proteins represent a major component of protoplasm, being involved in almost all natural processes that occur inside all the living cells. Proteins are non - soluble in different neutral salts (e.g.: NaCl, MgSO4) and are only dissolving once the salts are thinner. Unlike proteins, aminoacids are, most of them, water - soluble. The qualitative screening for aminoacids means that a colour change, precipitation or even ring formation can be noticed due to a transformation in the structural configuration after reacting with a chemical compound. In Table 4 are detailed the results of the studied samples, where "+" means present and "-" means that these components are absent.

Crt. no	Plant	Millon	Biuret	Xantoprotein	Ninhydrin	Cysteine
1	Sea buckthorn	+	+	+	+	+
2	Hyssop	-	+	-	+	+
3	Elderflower	+	+	+	+	+

Table 4. Qualitative screening for proteins and amino acids

4	Acacia	-	+	-	+	+
5	Cornflowers	+	+	+	+	+
6	Sorrel	-	-	-	-	-

As it can be observed from Table 4, in the case of Sorrel neither proteins nor aminoacids are present. Tyrosine is absent in aqueous extracts of Hyssop and Acacia, while in all the other extracts, proteins and aminoacids are clearly present.

## Qualitative screening for alkaloids

Alkaloids are those naturally present organic compounds that have a nitrogen atom in their structure. Their role in the plant metabolism are of protection against predators, nitrogen reservoirs and growth regulators [18]. Alkaloids were screened for using three different tests and the results are detailed in Table 5.

Crt. no	Plant	Mayer	Wagner	Hager
1	Sea buckthorn	-	-	-
2	Hyssop	+	+	+
3	Elderflower	+	+	+
4	Acacia	+	+	+
5	Cornflowers	+	+	+
6	Sorrel	++	++	++

Table 5. Qualitative screening for alkaloids

The qualitative screening revealed the total absence of alkaloids in Sea buckthorn and an abundance in Sorrel while in all the other studied samples they were moderately present.

### Quantitative determinations of phytocompounds

The quantitative determination of phytocompounds allowed an accurate determination of the total content of tannins, flavonoids and polyphenols by using spectrophotometric recordings at specific wavelengths (Table 6). The number of total tannins and flavonoids are calculated as mg catechin/L and the six aqueous extracts were analysed in triplicate. The total content of polyphenols has gallic acid's standard calibration curve. All the samples were analysed in triplicate.

Crt. no	Plant	ТСТ	TCF	ТСР
1	Sea buckthorn	169.333 mg/L	326.555 mg/L	502.102 mg/L
2	Hyssop	555.633 mg/L	956.369 mg/L	587.255 mg/L
3	Elderflower	599.065 mg/L	989.693 mg/L	689.555 mg/L
4	Acacia	523.852 mg/L	996.412 mg/L	605.333 mg/L
5	Cornflowers	602.410 mg/L	1055.321 mg/L	789.222 mg/L
6	Sorrel	799.878 mg/L	399.896 mg/L	656.555 mg/L

Table 6. Quantitative determinations of TCT, TCF and TCP

The results presented in Table 6 clearly show that all the plans have important amounts of polyphenoles, tannins and flavonoids and important information can be extracted:

• Cornflowers have the highest number of TCF (1055.321 mg/L), followed by Acacia (996.412 mg/L) and Elderflower (989.693 mg/L);

• the lowest value for TCF was recorded for Sea buckthorn;

• Sorrel has the highest recorded value of TCT (799.878 mg/L) while the lowest number for TCT was recorded for Sea buckthorn;

• Cornflowers have a TCP of 789.222 mg/L, followed by Elderflower and Sorrel.

#### Antioxidant activity

The DPPH assay is used to evaluate the presence of various antioxidants by spectrophotometry. This method relies on electron – transfer principle to produce a violet solution in ethanol and once an antioxidant in present shifts to colourless [19]. The results for the studied extracts are presented in Table 7.

Crt. no	Plant	AA, %
1	Sea buckthorn	88.33
2	Hyssop	89.58
3	Elderflower	90.90
4	Acacia	90.05
5	Cornflowers	89.95
6	Sorrel	88.00

Table 7. Antioxidant activity of the aqueous extracts

From the table above we can conclude that all the studied samples have excellent antioxidant activity, all the values are beyond 88.00 %, proving that the plants used in our experiments are full.

#### CONCLUSIONS

This research paper described the qualitative screening of phytochemicals and quantitative spectrophotometric determinations of different phytocompounds from plants known for their pharmacological benefits to human health: Sea buckthorn, Hyssop, Elderflower, Acacia, Cornflowers and Sorrel. Qualitative evaluation is based on different known analytical methods regarding the change in colour of the aqueous extracts prepared from plants once different reagents are added. All the aqueous extracts were prepared using the same protocol, by cold infusion under a controlled temperature, in the refrigerator, the only difference appeared in the colour of the resulted extracts that varied from orange (Sea buckthorn) to violet (Cornflowers) and in pH values that ranged from 6.5 to 7.2.

The qualitative screening for saponins revealed that all the samples contain important amounts of this phytocompound and the qualitative assay of flavonoids enabled us to conclude that all the flower-based aqueous extracts contain them. However, the qualitative evaluation of phenolic flavonoids showed that they are absent in all the studied aqueous extracts. Regarding the proteins and aminoacids, qualitative screening revealed their complete absence in Sorrel, while tyrosine is absent in aqueous extracts of Hyssop and Acacia. The qualitative screening revealed the absence of alkaloids in Sea buckthorn aqueous extract and an abundance in Sorrel while in all the other studied samples they were moderately present.

The quantitative determination of phytocompounds allowed an accurate determination of the total content of tannins (TCT), flavonoids (TCF) and polyphenols (TCP) by using spectrophotometric recordings at specific wavelengths: 500 nm for TCT, 510 nm for TCF and 765 nm for TCP. The results showed that Cornflowers have the highest number of TCF (1055.321 mg/L), followed by Acacia (996.412 mg/L) and Elderflower (989.693 mg/L), while Sea buckthorn exhibited the lowest calculated value for TCF. Regarding TCP, Sorrel has the highest recorded value of TCT (799.878 mg/L) while the lowest number for TCT was recorded for Sea buckthorn.

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# CONFERENCE PAPERS

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# PATHOGENESIS RELATED PROTEIN AND CORONATINE INSENSITIVE PROTEIN GENES IN RIBES SPP.

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#### EXTENDED ABSTRACT

#### **OVERVIEW**

In response to pathogen attack plants activate defense mechanisms including accumulation of salicylic acid (SA) and jasmonic acid (JA). Activity of *pathogenesis related protein* (*PR*) and *coronatine insensitive protein* (*COI*) genes in defense response pathways are established. *PRs* can act locally on pathogen or through enzymatic activity, generating signaling molecules that stimulate SA or JA defense pathways throughout the plant [1]. The *COI1*, which has been identified in insensitive to COR *A. thaliana* mutants, is involved in the JA signaling pathway and is required for resistance to insect herbivory and pathogens [2]. Recently, several researches have been conducted on SA and JA defense pathways in grapes, carrots, tomatoes, etc. However, genes and defense pathways related to pathogens resistance in *Ribes* spp. are unknown. The aim of this research is to establish *PR* and *COI* homologs for the studies of pathogenicity response to pathogens in blackcurrants (*R. nigrum* L.).

#### METHODS

Degenerate oligonucleotide primer pairs for detection of *PR* and *COI* were designed using Primer3plus programme [3] based on the most conservative parts of 18 and 22 nucleotide sequences obtained in National Center for Biotechnology Information (NCBI) database, respectively. Fragments of *PR* and *COI* genes in 8 *Ribes* species were amplified using polymerase chain reaction (PCR) and visualised in 1.3 % agarose gel. The amplified *R. nigrum* cDNA fragments were excised, purified, ligated into the pJET 1.2 blunt vector, cloned and sequenced on a 3130 Genetic Analyzer Gene Analyzer. The phylogenetic dendrogram was performed using PhyML programme; a bootstrap analysis with 100 replications was performed [4]. Percent identity matrix was created by Clustal2.1 programme.

#### RESULTS

After multiple sequences alignment, two primer pairs with degenerated nucleotides for detection of PR and COI were constructed. General information and properties of primers are compiled in table 1. Their application was performed in 8 *Ribes* species: *R. nigrum*, *R. americanum*, *R. pauciflorum*, *R. hudsonianum*, *R. sanguineum*, *R. glandulosum*, *R. dikusha*, *R. uva-crispa* and *Ribes* × *nidigrolaria* using PCR. Specific fragments of *PR* (392 bp) and *COI* (352 bp) were amplified in all tested species.

Primer	Orientation	Oligonucleotide sequences 5' to 3'	Temperature, °C	Length, bp
PRPd	Forward	GCMCARRAYWCHCCMCAAGAYT	- 63	392
	Reverse	TTGCCNSGDGGATCRTAAYTGCA		
COId	Forward	AGYCMAAAYGTRAGATGGATGCT	- 61	352
	Reverse	TTCTYKGWCCWGCHAGDGARTAR		

Table 1. Designed primer pairs for PR and COI detection

Seven heterogeneous sequences of *PR* have been identified in blackcurrants: PRP\_1, PRP\_2, PRP\_3, PRP\_4, PRP\_7, PRP\_8 and PRP\_9. Phylogenetic dendrogram of *Ribes PR* sequences shows their

arrangement into two branches at 100.0 % bootstrap (Figure 1A). First branch consisted of three sequences PRP\_1, PRP\_3, PRP\_9, homology between them 94.6 – 96.9 %. The remaining four homologs PRP\_8, PRP\_7, PRP\_2, PRP\_4 are genetically identical with each other 97.8 – 98.3 % and located in the second branch (Figure 1B).



Figure 1. Phylogenetic dendrogram (A) and percent identity matrix (B) of *PR* sequences identified in blackcurrants

The phylogenetic analysis of 7 *Ribes PR* and 18 other plant species *PR* sequences revealed the dependence on the *PR-1* and *PR-4* families. PRP\_1, PRP\_3, PRP\_9 belong to *PR-4*, which are associated with anti-fungal activities in plants [5]. Other 4 homologs – to *PR-1*, the expression of genes from this family is usable as molecular marker to indicate plant defence response [6].

Four heterogeneous sequences of *COI*: COI\_4.2.7, COI\_5, COI\_8 and COI\_9 have been sequenced from *R. nigrum* mRNA. The relationship of *Ribes COI* sequences was proved in phylogenetic dendrogram. Homologs divided into two groups at 83 % bootstrap (Figure 2A). The genetic identity 95.9 - 98.7 % between them was established (Figure 2B).



Figure 2. Phylogenetic dendrogram (A) and percent identity matrix (B) of *COI* sequences identified in blackcurrants

Multiple sequences and phylogenetic analysis confirmed that all *Ribes COI* homologs belong to the *COII* family and contain two leucine-rich repeat regions, which are antagonist of mitotic exit network protein 1-like subfamily. In phylogenetic tree of 22 plant species *COI* homologs, all *Ribes COI* homologs differed at 100.0 % bootstrap from others and formed an individual phylogenetic branch.

#### CONCLUSION

Newly designed primer pairs are suitable for the identification of *PR* and *COI* genes' homologs in *Ribes* species by PCR. The dependence of *Ribes PR* homologs to the *PR-1* and *PR-4* families and of *Ribes COI* homologs to *COI1* family were established.

Keywords: blackcurrant, gene homolog, degenerate primer pair

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# GLOBAL WARMING: DOES FREEZING TOLERANCE OF WINTER TYPE CROPS STILL MATTER?

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#### ABSTRACT

Winter type crops, sown in autumn, go through a complex process known as cold acclimation, which ultimately leads to the development of freezing tolerance. Cold acclimation has been shown to induce drastic changes in plant transcriptome, metabolome and physiology. Regardless, there is a gap in knowledge regarding the loss of freezing tolerance, also known as cold deacclimation, and the specifics of this process across various crop species and genotypes. Furthermore, global climate change is increasingly causing inconsistent temperature fluctuations and unpredictable weather patterns, thus disrupting cold acclimation or even inducing premature deacclimation in crops. Such phenomena can result in significant crop loss due to winterkill. The purpose of this article is to review the current state of knowledge on metabolites, genes and proteins related to cold acclimation and deacclimation in winter type crops, discuss the challenges climate change is posing to breeding efforts of freezing-tolerant crops, and examine the possible benefits of future research in this field. Due to global climate change, there is an emerging demand for crop varieties that are able to cold acclimate more reliably and retain their freezing tolerance during temperature fluctuations in winter. Current knowledge of freezing tolerancerelated metabolites and genes is scattered. Therefore, future studies should focus on linking metabolic traits and gene expression patterns to stable and improved freezing tolerance of winter type crops. The development of molecular markers related to freezing tolerance could accelerate breeding efforts of climate-resilient crops.

**Keywords**: abiotic stress, *Brassicaceae* spp., climate change, cold acclimation, deacclimation, *Poaceae* spp.

## **INTRODUCTION**

Winter type crops, usually sown in autumn, are unique in their ability to overwinter. They spend the cold season in a dormant state, and once temperatures increase, their vegetation is renewed and subsequently transitioned to the reproductive stage. These crops include such plants as wheat (*Triticum aestivum* L.), rye (*Secale cereale* L.), barley (*Hordeum vulgare* L.), oat (*Avena sativa* L.), rapeseed (*Brassica napus* L.), etc.. Winter type crops are known to attain higher yields, compared to spring type crops due to a more extensive root system and its resulting capacity to collect soil nitrogen [1]. However, insufficient winterhardiness is still the main limiting factor to achieve maximum yields in most temperate regions, as freezing temperatures can cause huge yield loss due to winterkill.

Winterhardiness is a complex trait, in which freezing tolerance, gained through the process, known as cold acclimation (or cold hardening), plays a significant role. Low autumn temperatures induce mechanisms of cold acclimation and eventually lead to efficient development of freezing tolerance [2]. Molecular mechanisms, active during cold acclimation, ensure the plant's survival from freezing temperatures, freezing-induced dehydration and ice crystal formation [3]. Temperature fluctuations and warm spells induce cold deacclimation (also known as dehardening), and thus, loss of freezing tolerance in crops. During the second half of winter, the molecular programming is reversed, and the plant is able to switch from dormancy to renewed growth and, eventually, its reproductive stage [4].
Nevertheless, global climate change is creating new demands for crop selection and raising questions regarding desired crop traits. One of these questions is, will freezing tolerance remain an important trait for overwintering crops in an increasingly warmer globe? This review will tackle this relevant question.

#### GAIN AND LOSS OF FREEZING TOLERANCE IN TIMES OF CHANGE

#### Cold acclimation and freezing tolerance in winter type crops

During autumn, winter type crops go through a complex process, known as cold acclimation. Cold acclimation plays a vital role in the formation of freezing tolerance, which in turn is one of the main components of winterhardiness in winter type crops. It occurs during autumn in low temperatures ranging from 0 to  $+10^{\circ}$ C. For winter wheat, the optimum time for cold acclimation saturation had been shown to be up to 8 weeks [2], however, the results highly vary depending on the temperature of cold acclimation and the genotype of the crops. Additionally, the acclimation threshold induction temperature had likewise been demonstrated to vary between disparate winter wheat varieties [5]. Moreover, levels of freezing tolerance display a wide range among different species, for example, winter canola had been shown to survive at  $-15^{\circ}$ C [6], some winter wheat genotypes can endure down to about  $-20^{\circ}$ C, whereas certain rye genotypes can survive temperatures down to  $-30^{\circ}$ C [7].

As cold acclimation occurs, simultaneously, a different process, known as vernalisation, takes place over 30-60 days. Once the vernalisation requirement is fulfilled and freezing tolerance decreases, as temperatures rise, the plant switches from the vegetative state to the reproductive state and, therefore, is able to induce flowering [8]. Although both cold acclimation and vernalisation occur during a similar period of time, they must not be confused, as these mechanisms ultimately lead to two different outcomes. Cold acclimation is crucial to survival in harsh winter conditions, whereas the eventual purpose of vernalisation is a timely induction of flowering. During the course of this period, specific genetic pathways, inducing dormancy, are activated and molecular changes, which delay flowering, occur. Vernalisation requirement in the *Triticae* tribe is determined by *Vrn-1* loci, found in homeologous group 5 chromosomes. However, *Vrn-1* loci were linked to *Frost resistance 1 (Fr-1)* loci, and were shown to significantly contribute to freezing tolerance [9,10,11]. The *Fr-2* locus, found on chromosome 5A had been demonstrated to code for 11 *CBF* genes, which are likewise important in acquisition of freezing tolerance [12].

During the course of winter, the plants experience numerous stresses, which involve not only low-temperature stress, but also freezing-induced dehydration, oxidative stress and the formation of ice crystals within the cells [7]. To avoid the detrimental effects of these factors, numerous molecular, biochemical, physiological and metabolic functions are altered in plants during cold acclimation [6,13]. Currently, only a single molecular cold-acclimation pathway had been studied extensively: the INDUCER OF CBF EXPRESSION–C-REPEAT-BINDING FACTOR–COLD REGULATED (ICE-CBF-COR) pathway [14,15]. Low temperatures activate the expression of *ICE* genes, which in response induce the upregulation of *CBF* genes. This cascade causes the eventual activation of *COR* transcription. Consequently, COR proteins protect plant cells from freezing-induced dehydration and freezing damage [15] (see Fig. 1).



Fig. 1. ICE-CBF-COR pathway. Low temperatures activate the transcription of INDUCER OF CBF EXPRESSION (ICE) transcription factor. By binding to the promoter region, it activates the transcription of another transcription factor, C-REPEAT-BINGING-FACTOR (CBF), which, in turn, promotes the eventual synthesis of COLD REGULATED (COR) proteins (adapted from [15]).

During cold acclimation, significant changes are seen at the gene expression level. A transcriptome study by Aleliūnas *et al.* (2020) had demonstrated that even short low temperature stress substantially affects the expression of over 2,400 nuclear genes in winter wheat [16]. According to Li *et al.* (2018), under natural conditions of cold acclimation, over 10,700 genes show significantly differential expression in winter wheat [13]. Similarly, micro RNAs (miRNAs), which function as RNA silencers and thus regulate gene expression, were found to play an important role in cold acclimation of winter type wheat and rapeseed [17,18].

Metabolic studies of cold acclimation in overwintering crops have likewise shown increased levels of carbohydrates (e. g. sucrose, fructose, raffinose) [6]; amino acids (such as proline and glycine betaine) [19]; proteins (e. g. antifreeze proteins and dehydrins) [6], as well as redox metabolites and enzymes (H<sub>2</sub>O<sub>2</sub>, NADH, NADPH, etc.) [20,21], lipids (fatty acids, sterols and phospholipids) [22], and upregulated transcription of genes, managing the production of these metabolites [13,23]. Furthermore, a proteomics study by Maryan *et al.* (2020) revealed that after early cold acclimation, *B. napus* leaves accumulate proteins, related to nitrogen metabolism, carbon metabolism, protein processing in the endoplasmic reticulum, biosynthesis of amino acids, and photosynthesis. Furthermore, the authors discuss the chloroplasts' susceptibility to cold and the oxidative stress it induces. To ensure the functioning and survival of the photosynthetic apparatus, molecular signalling is induced and thus, specific proteins, such as dehydrogenases, chaperonins and synthetases, are accumulated [24]. Therefore, currently, diverse groups of metabolites are known to be associated with cold acclimation and freezing tolerance in winter type crops (see Fig. 2).



Fig. 2. Metabolite groups, associated with freezing tolerance in winter type crops.

#### The elusive process of cold deacclimation

Cold deacclimation is a natural phenomenon, which can be relatively quickly induced by warming temperatures at the end of winter. Cold deacclimation gradually leads to loss of freezing tolerance in winter type crops – the entire process can take less than a week [4]. However, cold deacclimation can likewise be induced by temperature fluctuations in winter. The combination of reduced snow cover and premature warm spells can be severely detrimental to crop yield, if sudden extreme drops in temperature follow [25]. This mechanism is far less studied than cold acclimation, however, it is important to understand the molecular processes behind deacclimation to meet the growing demands of the agricultural industry under global climate change. Freezing tolerance had been demonstrated to peak in mid-winter – afterward, it decreases. This gradual decrease is caused by the loss of reserves, which the plants had accumulated for winter survival [26]. As this loss of freezing tolerance occurs, the dormancy period is over and growth is renewed. It had been shown in oilseed rape that once deacclimation takes place and elongation growth begins, the process becomes irreversible and repeated acclimation becomes impossible [27]. Earlier studies had likewise demonstrated that the expression of genes, responsible for the synthesis freeze-protective proteins, can only be induced during cold acclimation. As the plant switches from the vegetative to the reproductive stage, these genes are significantly down-regulated [28,29].

Vyse *et al.* (2019) analysed and compared 3 publicly available *A. thaliana* deacclimation transcriptomic data sets [30,31,32] to reveal 25 overlapping genes, which show increased transcription and 23 genes, which are down-regulated [33]. Among up-regulated genes were those, involved in growth and development, metabolism of phytohormones, and regulation of

cell water content. Down-regulated genes were related to accumulation of soluble carbohydrates and freezing tolerance-inducing proteins. As plants convert starches into soluble carbohydrates during cold acclimation, they do the opposite during deacclimation – increases in starch levels, required for renewed growth, have been observed [34]. Furthermore, levels of freezing-tolerance-associated dehydrins were found to decrease as freezing tolerance is lost [35]. These studies were carried out on *Populus* and *Hydrangea* genus species, respectively. However, similar changes were observed in winter oilseed rape [36] and winter wheat [6]. Currently, there is little research on metabolic changes during cold deacclimation in species of families *Poaceae* or *Brassicacea*.

#### Challenges imposed by global warming

Since the middle of the 20<sup>th</sup> century, the numbers of weather anomalies had been increasing. Compared to pre-industrial times, under the intermediate greenhouse gasses emission scenario, the global surface temperature is predicted to increase over  $1.5^{\circ}$ C by the end of this century. Under the worst scenario – this number could rise up to  $7.8^{\circ}$ C [37]. Furthermore, this increase in temperature may be more dramatic in the Baltic Sea region and Northern countries [38]. Warm temperature extremes are predicted to increase in frequency, whereas cold temperature extremes are likely to occur less often. Naturally, this raises the question – do we still need freezing tolerant winter crops?

Subzero winter temperatures can cause huge yield loss (in some Baltic Sea regions, up to 90%) due to winterkill [39], and without sufficient cold acclimation, crops can be extremely susceptible to freezing temperatures. Due to global warming, autumns are likely to become longer and warmer, thus, negatively affecting the crops' ability to cold acclimate by delaying the process itself. Once the temperature becomes sufficiently low to induce cold acclimation, the photoperiod will be significantly shortened, thus, reducing the length of photosynthesis and, consequently, the accumulation of carbohydrates, proteins, and other metabolites, required for freezing tolerance [40]. In a similar manner, increased clouding during autumn can likewise be detrimental to cold acclimation winter [40]. Another possible problem is the decrease of snow cover and its depth in winter. It is a well-known fact, that a sufficiently thick layer of snow cover (10-20 cm) acts as an insulator against extreme temperatures for winter type crops, therefore, as the protective layer becomes thinner or disappears altogether, the plants may suffer from freezing damage [41] (see Fig. 3).



Fig. 3. The possible effects of climate change on freezing tolerance of winter type crops.Warmer autumns, increased clouding and reduced photoperiod at the time of cold acclimation may diminish the effectiveness of photosynthesis, thus, reducing the crops' ability to accumulate metabolites, required for freezing tolerance. Decreased snow cover in winter may result in winterkill due to insufficient insulation from frost (adapted from [42]).

Additionally, the winter weather patterns are becoming less predictable and crops can be subjected to temperature fluctuations, such as repeated thaws, during which they deacclimate and lose their freezing tolerance prematurely [25,26]. These thaws can be followed by sudden extreme drops in temperature, which can cause winterkill if the plants are unable to properly reacclimate and regain their freezing tolerance in time [43]. Presently, there is a shortage of knowledge of metabolic profiles during cold acclimation regarding the impact of elevated temperatures and reduced duration of cold acclimation at autumn and its association to deacclimation and reacclimation in winter type crops.

# **CONCLUSIONS AND FUTURE PERSPECTIVES**

Currently, the only well-studied molecular mechanism, associated with cold acclimation, is ICE-CBF-COR. Numerous studies have described metabolites, such as soluble carbohydrates, freeze-protective proteins, amino acids and miRNAs, which increase in concentration during this process and contribute to freezing tolerance in winter type plants. Nevertheless, such information is scattered and future efforts are required not only to add to it, but also to join it into a comprehensible well-mapped entirety. Additionally, the mechanisms of winter crop cold deacclimation are not yet completely understood and there is a scarcity of studies regarding changes of metabolic profiles during such processes, especially in *Poaceae* and *Brassicaceae* species. There is a lack of knowledge, how higher temperatures and shortened length of cold acclimation during autumn affect the crops' ability to accumulate particular metabolite groups and what impact these factors have on freezing tolerance. Furthermore, it should be taken into consideration that significant differences could be found not only between different plant species, but also between genotypes within species.

Global warming will likely continue to provide unpredictable weather patterns, temperature fluctuations and extremes. These anomalies may detrimentally affect the plants' ability to cold acclimate, or even cause them to deacclimate prematurely. Subsequently, these factors may expose them to sudden unexpected freezing temperatures and cause significant yield loss. To accommodate the exponentially growing human population in the context of increasingly unpredictable global climate change, new and improved varieties of climate-resilient crops are required. These efforts will demand thorough knowledge of molecular dynamics during cold acclimation and deacclimation at both transcriptomic and metabolomic levels. Specific metabolic traits and gene expression patterns must be linked to increased and retained freezing tolerance in winter type crops. Once this gap in knowledge is bridged, the genes, responsible for the biosynthesis of such metabolites, can be clarified and used as markers for effective future selection of crops.

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#### ABSTRACT

The biggest damage to *Rosaceae* family stone and pome fruit plants is caused by brown rot disease (Monilinia spp.). There are four main world widespread Monilinia spp. pathogens: M. laxa and M. fructigena – commonly found in Europe; M. polystroma spread in Japan, expanding in Europe and USA; *M. fructicola* is indigenous in the USA and Australia, already found in Europe, where this pathogen is assigned to quarantine pathogens list. Simple sequence repeats (SSR) are a suitable tool for discovering genetic diversity and for tracking the epidemic of this disease, but it requires priori knowledge about genomic data. Therefore, up until now only four SSR markers are available for M. fructicola and one for M. laxa. Since 2019, all Monilinia spp. genomes are available in the National Center for Biotechnology Information (NCBI) GenBank database at scaffold or contigs level, it is possible to develop genome-wide SSR markers. During this study M. fructicola, M. fructigena, and M. laxa reference genomes were analysed using Genome-wide Microsatellite Analyzing Tool Package (GMATA) for the development of SSR markers. In total 15 788 SSR motifs of the whole M. fructicola genome were found, 11 091 and 12 337 of M. fructigena and of M. laxa genome, respectively. In total 81.7% of them were assigned as markers and the primers as well melting temperatures for them were provided. For identification of the species-specific markers in silico polymerase chain reaction was conducted. The structure of SSR motives were analyzed - in all three species dimers are dominating (more than 41.5%). The most abundant SSR motives for all the species are TA and AT; in M. fructicola they comprise 28.6 % of all motives, in M. fructigena - 22.1%, and M. laxa - 33.3%. Such markers would be useful for the intraspecific and interspecific genetic diversity studies of Monilinia spp.

#### **Keywords:**

Brown rot, genomes, genomic-wide, Monilinia spp., SSR motifs, SSR markers,

#### **INTRODUCTION**

Pome and stone fruit plants play an important role in fruit production all over the world. The biggest damage to fruit plants is made by fungal diseases [1]. The most important disease caused by fungal *Monilinia* spp. pathogens for *Rosaceae* family plats is brown rot [2]. Brown rot reduces the fruit quality in pre- and post-harvest stages [3]. In Europe, *Monilinia* spp. pathogens cause 7 - 15% of yield losses during the vegetation period and 0.6 - 8% during storage of the harvest. These pathogens infect fruit plats during the whole vegetation period - it causes blossom, leaf blight and, also, affects fruits [4].

Brown rot is caused by four mains related *Monilinia* spp. species: *Monilinia fructigena* Honey, *Monilinia laxa* (Aderh and Ruhland) Honey, *Monilia polystroma* (G. Leeuwen) L. M. Kohn and *Monilinia fructicola* (G. Winter) Honey [5]. The spread in the world of *Monilinia* spp. pathogens depend on the geographical location (continent) and the host plant [1]. *M. fructigena* is the main pathogen in Europe, which mostly causes brown rot in the pome fruits. In North America and Australia, this pathogen is on the list of quarantine pathogens [6].

*Monilinia laxa* causes the brown rot blossom blight disease, it is spread in California, Europe, South Africa, and Chile [2, 7]. *M. polystroma* is still rare in Europe, but already identified in the Czech Republic [8], Hungary [9], Poland [10], and Italy [11]. Morphologically *M. polystroma* pathogen is similar to *M. fructigena*, its country of origin is Japan [12]. *M. fructicola* is originally found in North and South America and New Zealand, but currently, it is also spreading to other geographical territories [1]. In Europe and Mediterranean regions, this pathogen is on the list of European and Mediterranean Plant Protection Organization (EPPO) database as an A2 category quarantine pathogen. *M. fructicola* is already found in Germany, Italy, Slovenia, Switzerland, Croatia, France, Hungary, Greece, Montenegro, Serbia, Span, Azerbaijan, and Romania [8]. *Monilinia* spp. pathogens are spreading all around the world by natural spore dispersion in the environment and during the importation of the fruits to the countries quite fast. It is important to track the disease epidemics and genetic variations in the world [13].

For the inter and intraspecific species genetic differentiation analysis molecular markers can be used [14]. Microsatellite (simple sequence repeat (SSR)) are tandem repeats of deoxyribonucleic acid (DNA) units flanked by unique left and right sequences in the genome. Microsatellite markers are polymorphic, co-dominant, polymerase chain reaction (PCR) -based, and multi-allelic. The mutation rate of SSRs depends on the length of the repeat units [13, 15]. SSR method is widely used in breeding, selection, and other research, as this method is highly versatile, cheaper than other methods, and easy to use [16]. Due to these properties, microsatellite markers can be applied in a wide range of fields and are more often chosen than other genetic markers (e.g., SNP, RFLP, AFLP, and others) [15].

Only four SSR primer pairs have been developed for *M. fructicola* pathogen and one for *M. laxa* [13]. Therefore, there is a demand for more markers to be available for *Monilinia* spp. genetic diversity and pathogenicity analysis.

For the development of microsatellite markers, *a priori* the information about the DNA sequences is required, that is why the conventional methods using genomic libraries for SSR screening are expensive and time-consuming [15]. In 2019, the genomes of *Monilinia* spp. were sequenced using next-generation sequencing platforms and are available in National Center for Biotechnology Information (NCBI) database [20]. The announced reference sequences of the pathogens are in scaffolds or contigs level: *Monilinia fructigena* - 1,089 scaffolds [17], *M. laxa* – 49 contigs [18]. and *M. fructicola* – 20 contigs [19]. The performance of sequenced *Monilinia* spp. genomes encourage the analysis of the pathogens at the genomic level and can be used for more effective development of SSR markers [19].

Fungal *Monilinia* spp. pathogen species originally found in different continents, but due to of natural spread and commercial fruit import, the pathogens expand to other countries and their genetic prevalence becomes much more diverse. Newly introduced pathogens are changing the composition and genetic diversity levels of existing species and increase fruit losses [1]. Information about *Monilinia* spp. genomic-wide SSR distribution would encourage genetic diversity analysis and help to track the pathogenicity of the disease.

The study was aimed for identification of genome-wide SSR motifs and development of SSR marker of *Monilinia* spp. for three *Monilinia* species: *M. fructigena, M. fruicticola,* and *M. laxa*.

# MATERIALS AND METHODS

#### 1.1. Data Collection

The genome assemblies of *Monilinia fructigena* [17], *M. laxa* [18] and *M. fructicola* [19] were downloaded from National Center for Biotechnology Information (NCBI) genomes

database [20]. *M. fructigena* was assembled scaffold–wise, *M. laxa* and *M. fructicola* assembled in cotings level (Table 1).

Species	Genome assembly	Genome size	Assembly level	Scaffold/contig
M. Fructicola	ASM869222v1	44.048	Contig	20
M. Fructigena	ASM367162v1	39.329	Scaffold	1 089
M. Laxa	ASM929945v1	42.815	Contig	49

Table 1. The genomic data of different Monilinia spp.

# **1.2.** Markers and Development

For the identification of the microsatellite motifs and design of the SSR markers and primer sequences, Genome-wide Microsatellite Analysing Toward Application (GMATA) program was used [16]. During the research four modules of the program were used (Fig.1): (1) SSR identification, (2) SSR statistical analysis and plotting, (3) Marker designing (uses Primer3 algorithm in GMATA) and (4) *in silico* polymerase chain reaction (e-Mapping). The parameters for GMATA program modules were chosen: for SSR identification minimum length of motifs were 2, maximum length – 6, minimal repeat-times of the motifs were 5; for SSR statistical plotting, marker design, and for *in silico* polymerase chain reaction (e-Mapping) the parameters were left standard.



Fig.1 Flow chart describing the analysis of Monilinia spp. genome-wide microsatellite markers.

#### **RESULTS AND DISCUSSION**

#### **1.3.** Development of SSRs for *Monilinia* spp.

For the development of the Monilinia spp. SSR markers, SSR motives were found successfully, using the GMATA platform. A total of 39 216 microsatellites motifs were identified from the genomes of three Monilinia spp. species. The highest number of microsatellites motifs were identified in *M. fructicola* (15 788), followed by *M. laxa* (12 337) and *M. fructigena* (11 091) (Table 2). *M. fructicola* has the largest genome (44.048 Mbp) from all Monilinia spp., the highest number of total SSR number and the SSR density is also the highest (Fig. 2). In fungi species, the SSR motifs abundance directly dependent from genome size [21].

A relationship between the total SSR motif number in the species and the genome size This relationship was confirmed by the researchers, of some was observed. Ascomycota division species: Fusarium graminearum, Magnaporthe grisea, and Neurospora crassa, where the Magnaporthe grisea has the biggest genome and the highest number of SSR motifs, but Aspergillus nidulans has the smallest genome of all Ascomycota division, however, the SSR motif number is higher than *Fusarium graminearum* [22]. This relation depends on the observed species number - having more species, deviation from this relation occurs.

The genome sizes of 4 other Ascomycota division species are smaller than Monilinia spp. genomes but the number of identified microsatellites in M. grisea (15 751) is close to M. fructicola (15 788). However, the average SSR density of these four species is smaller (275.8 in average) than Monilinia spp. (309.7 in average) [22]. Analysis of different Ascomycota division species had shown that Monilinia spp. has the largest genome and the highest number of identified SSRs.







#### 1.4. Characterization of SSR motives and the development of markers

In all three *Monilinia* spp. species *M. fructicola* (7 178), *M. fructigena* (4 590), *M. laxa* (6 036) dimer motifs are most abundant, followed by trimer, tetramer, pentamer, and hexamer (Fig. 3). Among all the *Monilinia* spp., the highest number of dimer motifs were found in *M. fructicola* (7 178), followed by *M. laxa* (6 036) and *M. fructigena* (4 590). In the case of trimer repeats, the highest number was observed also in *M. fructicola* (3 381), followed by *M. laxa* (2 113). The number of tetramer motifs is similar to trimer: the highest number is in *M. fructicola* (3 096), followed by *M. fructigena* (2 220) and *M. laxa* (1 814). In *M. fructicola* the most abundant SSR motifs are the pentamer (1 232), followed by *M. laxa* (1 192) and *M. fructigena* (1 000). The highest number of hexamer motifs are in *M. laxa* (1 182), followed by *M. fructicola* (899) and *M. fructigena* (868) (Fig. 3).

In all three *Monilinia* species, dimer structure for SSR motives are dominating (45.3%), following by trimers – 19.5%, tetramers – 18.7%, however, the pentamers (8.8%) and hexamers (7.7%) are the least common in the genomes. In *Monilinia* spp. pathogens, the most abundant motif of SSR is a dimer, however other research has reported, that in *Ascomycota* division, *A. nidulans, F. graminearum, M. grisea and N. crassa* species dimer repeats in the genomes were the least common [22]. However, in the *A. anomala* dimer motifs are abundant right after the monomers and the following motifs are trimer and tetramer [23]. According to microsatellites k-mer distribution *Monilinia* spp. is the most similar to *A. anomala*.



Fig.3. K-mer distribution of microsatellite motifs in the Monilinia spp. genomes.

In the *Monilinia* spp. genomes TA and AT SSR motifs are the most abundant (Fig. 4). In the *M. fructicola* and *M. laxa* pathogens, TA motifs are the most commonly found (15 % and 18.2 % accordingly). In the *M. fructigena* AT SSR motif is the most abundant (11.2 %). In the research of seven fungi species (*Aspergillus nidulans, Coprinus cinereus, Cryptococcus neoformans serotype A, Fusarium graminearum, Magnaporthe grisea, Neurospora crassa, Ustilago maydis*), AG, AT, and AC repeats are the most frequent. In *Ascomycota* division *A. nidulans* species, the most abundant motif is AT, this report coincides with *M. fructigena* pathogen. However, TA SSR motif, which is the most frequent in *M. fructicola* and *M. laxa* pathogens, is not noticeable in other fungi species [22].



Fig.4. Distribution of SSR motives in Monilinia spp.

The top distribution of SSR length fluctuates between 10 - 36 base pairs (Fig. 5). The most common SSR length for all three *Monilinia* spp. is 10 bp, followed by 20 bp in *M*. *fructicola* and *M. fructigena* and 12 bp in *M. laxa*. Other research has reported that the preferred SSR length for fungi is 20 bp approximately [21]. In *M. fructicola* genome 25.8 % of all top distributed SSR lengths are more than 20 bp, in *M. fructigena* genome - 26.6 %, and in *M. laxa* – 25.3 %. Approximately, a quarter of all top distributed SSR lengths are well preferred. The longest top SSR motifs are 30 - 36 bp, the biggest percent of long motives are reported in *M. laxa* pathogen. It was proposed, that for longer microsatellite sequences, the differences between fungal species are higher. It is determined by the mutation rate, which is species-specific and size-dependent [22]. These microsatellites are suitable not just for intraspecific species genetic diversity research, but also for interspecific analysis.



During this study 26 366 markers were designed for *Monilinia* species: 9 754 for *M. fructicola*, 8 506 – *M. fructigena*, and 8 106 for *M. laxa* SSR sequences. For the identification of species-specific markers, an *in silico* PCR was conducted (ePCR module in GMATA program). 98.6% designed markers for *M. fructicola* were specific for this species, 96.3 % - specific for *M. fructigena*, and 96.0% for *M. laxa* pathogen (Table 3). Until now, there is just 1

SSR marker developed for *M. laxa* pathogen and 4 for *M. fructicola* [13]. The SSR marker CHML5, developed for *M. laxa* pathogen (CTCTTCTTC)<sub>6</sub> repeat, was not detected during our research. This is probably due to GMATA program limitations as the highest number of k-mer was 6. Therefore such sequence was identificated as trimer repeat (CTT)<sub>2</sub> within GMATA program. For *M. fructicola* pathogen CHMFc4 marker reverse primer sequence [13] and SSR motif (GAGAGAT)<sub>4</sub> were successfully identified in our developed markers. The detection of more genome-wide markers depends on the parameters of the program – amplicon settings, flanking sequence length, and others.

Species	<b>Designed markers</b>	Species-specific markers
M. fructicola	9 754	9 617 (98.6%)
M. fructigena	8 506	8 188 (96.3%)
M. laxa	8 106	7 781 (96.0%)

Table 3. Designed markers for Monilinia spp. SSR motifs.

# CONCLUSIONS

1. 39 216 microsatellite motifs are distributed in *M. fructicola*, *M. fructigena*, *M. laxa* genome-wide.

2. The most abundant SSR motifs for *Monilinia* spp. were dimers (45.3%), followed by trimers, tetramers, pentamers, and hexamers.

3. TA and AT motifs are the most frequent for *Monilinia* species.

4. For microsatellites of *Monilinia* spp. pathogens, 26 366 markers were developed, 97% of the markers were specific for *M. fructigena*, *M. fructicola*, *M. laxa* species, which can be used for intraspecific and interspecific species genetic diversity analysis.

# **ACKNOWLEDGEMENTS**

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# SCREENING OF THE SSR LOCI SET FOR POOLED SAMPLE ANALYSIS OF SCOTS PINE SEED LOTS

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#### ABSTRACT

Forest seed orchards are one of the main sources of obtaining seeds with high hereditary traits for reforestation purposes. Genetic structure of seed orchards is the main factor influencing on the formation of hereditary characteristics of seed progeny. Among the additional factors that have a significant impact on the formation of the genetic structure of seed lots, the mating system is assigned a significant role. One of the advanced techniques for studying and evaluation the mating system is the use of molecular genetics assay, that in turn requires the development of a set of informative DNA markers and methodology. The paper presents results of the new approach design for seed lots genetic structure assay. Investigation of DNA marker set allowed to select ten highly informative (for molecular genetic analysis of seed lots) microsatellite loci localized in the cell nucleus: Pttx 4001, Pttx 4011, Pttx 3116, Psyl 2, Psyl 16, Psyl 17, Psyl 18, Psyl 36, Psyl 42, Psyl 44. The results of the electrophoretic spectra analysis, comparative assessment of individual and pooled samples assay and calculation of the genetic structure of the seed lot are presented. It is shown that the developed method is similar in analytical characteristics to the traditional approach, but cheaper in cost and superior in performance.

Keywords: seed orchards, molecular genetic analysis, genetic variation, Scotch pine, SSR loci.

#### **1. INTRODUCTION**

Today, in addition to the tasks of increasing the productivity of forest seed orchards and improving the sowing qualities of harvested seed material, much attention is paid to genetic and breeding issues devoted to the preservation and reproduction of genetic resources of species, the degree of manifestation of economically valuable traits, an increase in the adaptive potential of plants, etc. [1].

An assessment of seed progeny genetic structure, makes it possible to establish not only the effective number of the ramets (or clones) in seed orchards (a set of maternal and paternal trees directly involved in the formation of seeds), but also to describe mating system in it. Subsequent analysis of the genetic structure of the pollen pool, compatibility and prevalence of various variants of genotypic combinations makes it possible to optimize the clonal structure of seed orchards based on the aspects of their reproductive combination [2].

Despite the presence of a significant number of methods for molecular genetic assay of living organisms, studies of the mating system in forest seed orchards were limited, that was caused by lack of informative, but relatively inexpensive methods for analyzing seed offspring. One of the approaches for assessing the hereditary characteristics of forest seed orchards, certification and inventory of clones of maternal trees, determining their genetic relationship and the genetic diversity of the seed lots, is the DNA assay. The suitability of molecular genetic markers for certain types of research is mainly determined by their information content, which in turn determines a number of requirements for them: a high level of polymorphism; the codominant type of the inheritance; a certain (in relation to the tasks being solved) location (or distribution) in the genome [3].

Recently, due to the development of innovative methods of DNA assay, in the study of biological objects of small size (microbiomes, colonies of small insects, etc.), more attention is paid to the simultaneous analysis of all individuals present in the sample. It allows to reduce

the cost of analysis significantly, increase productivity and reduce time costs, and the obtained data show the actual genetic structure without using methods of statistical synthesis and extrapolation.

Based on the objectives of the research, screening of microsatellite loci set in the seed orchard of Scots pine was carried out for the subsequent selection of SSR-markers with the highest level of polymorphism, as well as a pooled samples method for the analysis of seed lots was developed and its diagnostic efficiency was assessed.

# 2. MATERIALS AND METHODS

The collection of experimental material for analysis was carried out in block No. 1 of the Scots pine seed orchard (II generation, year of foundation 2002, area 3,0 ha), located on the territory of Staro-Dyatlovichsky forest region (quarters 44, 45) of the Gomel forest enterprise. In the study area, 128 Scots pine trees samples were collected for research (Figures 1.).

*17/	*54/	*28/	*11/	<u>*85a/</u>	*17/	*29/	*17/	*5/	*11/	*17/	*54/	<u>*//</u>	*11/	*85a/	*11/	*11/	*17/	*58/	*76/	<u>*11/</u>	*67/	*28/
1570	597	427	/09-2	913	1363	031	749	1-1	<u>/0/a-2</u>	1552	597	40	10/a-2	513	709-2	/0/a-2	749	145	857	/0/a-2	510	427
*84/	*85/	*67/	*32/	*84/	*54/	*28/	*20/	*11/	<u>*17</u>	*28/	*85a/	*6/	*58/	*84/	*54/	*46/	*58/	*11/	*58/	*6/	*36/	*10/
455	920	510	420	445	597	<u>519-2</u>	033	719	10	519-2	520	343	47-5	445	349	632	437	/18	400	347	910	737-1
*58/	*58/	*67/	*32/	*11/	*58/	*58/	*85a/	*85a/	*85a/	*58/	*8/	*17/	*28/	*20/	*58/	*20/	*85a/	<u>*85a/</u>	*11/	*28/	*10/	*11/
475	461	517	415	<u>707a-2</u>	438	457	936	913	910	457	891	30	422	370	366	366	936	913	719	522	737-3	<u>70/a-2</u>
*5/	*17/	*11/	*20/	*32/	*67/	*84/	*11/	*20/	*28/	*11/	*17/	*20/	*20/	*28/	*11/	*84/	*11/	*28/	*11/	*57/	*85a/	*28/
13	1505	<u>/0/a-2</u>	505	418	513	455	10/a-2	323	530	10/a-2	1505	500	505	423	10/-1	455	718	523	10/a-2	597	913	523
*28/	*28/	*28/	*28/	*28/	*28/	*28/	*58/	*28/	*28/	*28/	*28/	*28/	*28/	*28/	*28/	*28/	*67/	*28/	*28/	*85a/	*5/	*28/
533	423	529	521	522	523	524	527	424	427	423	533	529	521	522	523	524	510	424	427	936	0	524
*17/	*54/	*28/	*28/	*85a/	*56/	*67/	*17/	*82/	*51/	*17/	*54/	*28/	*28/	*85a/	*56/	*67/	<u>*17/</u>	*82/	*20/	*17/	*54/	*11/
1570	597	427	530	913	331	517	749	779	373	1570	597	427	530	913	337	517	46	719	570	1570	597	719
*84/	*85/	*67/	*32/	*84/	*54/	*46/	*58/	*11/	*58/	*11/	*85/	*67/	*32/	*84/	*54/	*46/	*28/	*11/	*58/	*84/	*85/	*67/
455	920	510	420	445	597	632	437	719	466	<u>707a-2</u>	920	510	420	445	597	632	533	719	466	455	920	510
*58/	*58/	*67/	*32/	*20/	*58/	*57/	*85a/	*85a/	*85a/	*58/	*58/	*67/	*28/	*20/	*59/	*57/	*85a/	*85a/	*85a/	*58/	*58/	*67/
475	461	517	415	579	457	597	936	913	910	475	461	517	523	579	458	597	936	913	910	475	461	517
*5/	*17/	*20/	*20/	*32/	*67/	*84/	*11/	*11/	*28/	*5/	*17/	*20/	*20/	*17/	*67/	*84/	*11/	*28/	*28/	*5/	*28/	*20/
13	1565	566	565	418	513	455	718	707a-2	530	13	1565	566	565	46	513	455	719	523	536	13	524	566
*28/	*28/	*28/	*28/	*28/	*28/	*28/	*58/	*28/	*28/	*28/	*28/	*28/	*46/	*28/	*28/	*28/	*45/	*28/	*28/	*85a/	*28/	*28/
523	423	529	521	522	523	524	527	424	427	423	533	529	706	522	523	524	814	424	427	936	423	529
*17/	*54/	*28/	*28/	*85a/	*56/	*67/	*17/	*82/	*28/	*17/	*54/	*28/	*28/	*85a/	*28/	*67/	*17/	*82/	*51/	<u>*17/</u>	*54/	*28/
1570	597	427	530	913	331	517	749	779	524	1570	597	427	530	913	529	517	749	719	373	46	597	427
*84/	*85/	*67/	*32/	*84/	*54/	*46/	*58/	*11/	*55/	*84/	*85/	*67/	*32/	*84/	*54/	*46/	*58/	*11/	*28/	*84/	*85/	*67/
455	920	510	420	445	597	632	437	719	67	455	920	510	420	445	597	632	457	719	523	455	920	510
*58/	*11/	*67/	*32/	*20/	*58/	*28/	*85a/	*85a/	*45/	*58/	*58/	*67/	*32/	*20/	*59/	*57/	*85a/	*85a/	*85a/	*58/	*58/	*67/
475	707a-2	517	415	579	457	423	936	913	814	475	461	517	415	579	458	597	936	913	910	475	461	517
*5/	*17/	*20/	*20/	*32/	*67/	*84/	*11/	*25/	*28/	*5/	*17/	*20/	*20/	*32/	*67/	*84/	*11/	*28/	*28/	*57/	*85a/	*28/
13	1565	566	565	418	513	455	718	523	530	13	1565	566	565	418	513	455	718	523	536	597	913	523
*28/	*28/	*28/	*28/	*28/	*28/	*28/	*58/	*28/	*28/	*28/	*28/	*28/	*28/	*67/	*28/	*28/	*28/	*28/	*28/	*85a/	*28/	*28/
533	423	529	521	522	523	524	527	424	427	533	423	529	521	513	523	524	536	424	427	936	423	529
<u>*28/</u> 423	допо	олненн	ые кло	ны																		



Biological samples were needles and 30 cones from the upper and lower parts of the crown of each studied pine tree (clone). The seeds were extracted from the cones and each group of analyzed seed lots was represented by the seed samples obtained from individual cone.

The samples for the molecular genetic assays were the needles from maternal tree and 7day-old seedlings obtained in the Jacobsen apparatus 5101 Series (RUMed, Germany) at a temperature of 25 °C. DNA isolation from pine needles and seedlings was carried out by CTAB protocol [4]. Samples intended for individual genotyping were placed in separate microcentrifuge tubes, for group analysis plant samples were combined together. Fragments of seedlings intended for pooled samples genotyping were characterized by similar diameters and locations in seedlings. The DNA samples were diluted to the same concentration – 30 ng/ $\mu$ L.

Set of microsatellite sequences of nuclear DNA were used [5].

Molecular genetic assay consisted of the following stages: DNA extraction; amplification of marker loci; electrophoresis; comparative analysis of the results of individual and group genotyping.

Preliminary electrophoresis was carried out in a 2% agarose gel. The final electrophoretic assay of PCR amplicons was performed using an ABI Prism 3500 genetic analyzer (Thermo Fisher Scientific, USA) according to the manufacturer's recommended protocol [6]. The results

were analysed using the GeneMapper 4.1 software package (Thermo Fisher Scientific, USA). Alleles were designated by the name of the analysed locus and the size of the band (in nucleotide bases).

# **RESULTS AND DISCUSSION**

Based on the above stated purpose of the research, we selected ten microsatellite loci. PCR amplification of ten microsatellite loci revealed 69 allelic variants. For loci, varying degrees of polymorphism were found. The least variables were Psyl44 and Psyl18 (3 alleles), Psyl42, Psyl44 (4 alleles), the most polymorphic was the PtTx4001 locus (13 alleles). The rest of the loci showed moderate polymorphism: Psyl17, Psyl2 - 6 alleles, Psyl36, Psyl16 - 7 alleles, and PtTx4011 – 9 allelic variants. The list of allelic variants and their characteristics are presented in Table 1

Locus	Repeat type	Identified alleles	Main alleles				
Psyl44	(CGG)5	172*; 177; 182*	177 (95%)				
Psyl18	(GCA)7	292; 294; 300; 302	294 (90%)				
Psyl42	(TC) <sub>9</sub>	168; 172; 174; 176	174 (40%); 168 (30%)				
Psyl17	(TA) <sub>7</sub>	215; 217; 219; 221; 225; 227	219 (40%)				
Psyl2	$(GCT)_5$	196; 201*; 202; 204; 206; 207*	204 (85%)				
Psyl36	(GTC) <sub>7</sub>	239; 245; 248*; 251; 253; 254*; 257	251 (80%)				
Psyl16	(AT)7	201; 203; 205; 208; 210; 212; 214	203 (30%); 205 (30%); 210				
			(20%)				
PtTx 4011	(CA) <sub>20</sub>	244; 260; 261*; 262; 264; 265*; 267*;	261 (25%); 262 (25%); 264				
		268; 280	(25%)				
PtTx 4001	(CA) <sub>15</sub>	202; 202; 206; 208; 210; 212; 214; 216;	216 (40%)				
		218; 220; 222; 224; 228					
PtTx 3116	(TTG)7- (TTG)5	154; 157; 160; 162; 166; 173	154 (50%); 160 (20%); 166				
			(20%)				
* - polymorphism not associated with variation of the tandem repeat number							

Table 1. Main characteristics of the studied Scots pine SSR loci

Interpretation of the obtained electrophoretic data was reduced to the description of microsatellite spectra taking into account the size of each identified allomorph (projection of the peak apex on the X axis, expressed in nucleotide bases) and its amount (projection of the peak apex on the Y axis, peaks height share in spectra) in the form of tabular and graphical data (Fig. 2).





Fig. 2. Electrophoretic spectrum of the combined sample of Scots pine seeds at the Psyl17 locus: primary (left) and graphical (right) data

A quantitative assessment of the electrophoretic spectra of samples represented by individual seeds showed, that, in most cases, the heights of the peaks of different allomorphs (in the case of heterozygous genotypes), differed from the 1:1 ratio, which is most likely due to

variation in the PCR efficiency coefficients for different alleles. At the same time, the reproducibility of the structure of the spectra in similar genotypes was absolute and did not depend on external factors (Fig. 3). The obtained data on the peculiarities of PCR amplification of various allelic variants made it possible for each locus to calculate correction factors for interpreting the results of electrophoretic assay.



Fig. 3 Electrophoretic spectra of individual Scots pine seedlings

Verification of the seed lot genotyping was carried out by comparing with genetic data obtained from the analysis of separate seedlings (Figures 4). As can be seen from Figure 4, the results obtained using the two alternative approaches were broadly similar. Differences (the absolute value) in the frequencies of allelic variants did not exceed 5%. At the same time, the error (the relative value) in calculating the frequency of occurrence could vary from 6% (not rare alleles) to 33% (rare alleles).



Fig. 4 Genetic profile of sample 28/529-2, calculated based on the analysis of separate seedlings (left) and the pooled sample (right)

During the detailed analysis of SSR-spectra, it was found that the electrophoretic features were similar to the results obtained by PCR amplification of individual seedlings. The maximum allowable number of simultaneously analysed haplotypes was 20, which made it possible to identify alleles with a frequency of occurrence  $\geq 5\%$ . Direct determination of the genotype of the maternal trees and the genetic structure of the pollen pool based on the obtained metadata in the case of highly polymorphic loci (He  $\geq 0.75$ ) was impossible (Figures 4) and required additional molecular genetic assay of the maternal trees. At the same time, in the case of loci with a moderate level of polymorphism (He  $\leq 0.30$ ), the genotype of the maternal and paternal trees could be calculated based on the data of the pooled sample analysis. In the case of establishing the frequencies of the alleles in the pollen pool, it was possible to calculate the degree of genetic differentiation between the samples according to the algorithms described in [7].

<sup>(</sup>Psyl17 locus, genotype 219/221)

#### CONCLUSION

Amplification of the ten microsatellite loci was carried out and 69 allelic variants were identified. Based on the results obtained, it was found that among the studied microsatellite loci, Psyl16, PtTx 4011 and PtTx 4001 have the highest level of polymorphism, which determines their high degree of information content for further research on the assessment of mating system in seed orchard.

A pooled sample method has been developed for the analysis of Scots pine seed lots. It was found that the values of the main diagnostic parameters of the method are similar to the analysis based on the study of individuals separately. The permissible error in calculating the frequency of occurrence of allelic variants did not exceed 5% (the absolute value). The use of this technique is suitable for the certification of maternal trees and the calculation of the pollen pool genetic structure.

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# **REGIONAL CLIMATE MODELS DATA ADAPTATION FOR THE PROJECTION OF THE LITHUANIAN RIVERS RUNOFF**

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#### ABSTRACT

The Lithuanian Government has prepared National Energy and Climate Plan (NECP) for the period 2021-2030. This NECP is planning the expansion of renewable energy sources up to 45% in the energy mix. In order to properly and productively operate hydropower plants in the conditions of climate change, it is necessary to project the future runoff of rivers, if it is lower than the environmental (95% probability), it let us plan measures for the HPP performance optimization. For this research we applying hydrological modelling based on climate models and emission scenarios. The First Intergovernmental Panel on Climate Change (IPCC) identified the effects of global warming caused by anthropogenic greenhouse gases. Nowadays, there are five IPCC reports produced with many climate change scenarios for different climate models and emissions scenarios. According to Fifth Assessment Report (AR5), air temperature could rise from 1 to 4 degrees in 21th century. It will affect hydrological riverine regime (e.g. runoff) and hydroenergy resources. Changes of resources could be assessed by hydrological modelling of riverine catchment according to different climate scenarios. The daily precipitation and air temperature of 16 Lithuanian meteorological stations were the initial data for this research. The reference period of 1986-2005 was selected. Output (projections of precipitation and air temperature) of three regional climate models (ICHEC-EC-EARTH, MOHC-HadGEM2-ES, and MPI-M-MPI-ESM-LR) generated by three most commonly used RCP scenarios (RCP2.6, RCP4.5, and RCP8.5) for the periods of near (2021-2040) and far (2081-2100) future.

Keywords: climate change, RCP, regional climate models.

#### **INTRODUCTION**

Mitchell (1953) [1] was one of the first to use the term *Climatic Change*, when he was looking for answer on the multiannual rise in the average air temperature. In the official definition of climate change, it is classified as anthropogenic changes in the composition of the global atmosphere observed over a comparable period [2]. In scientific research, climate change is usually evaluated through changes in temperature T and precipitation P, which influence the hydrological cycle and, consequently, river runoff. Analysis of Lithuanian rivers in recent decades shows that the most significant changes in runoff increase occur during the winter season and decrease during the spring, with the least changes occurring during the spring and summer season [3], [4]. In the winter season, the runoff will increase and in the spring season it will decrease according to all emission scenarios. The emission scenarios have much bigger influence on forecasting of the Nemunas River runoff than the global climate models [5].

The global temperature is estimated to rise by  $0.5 \,^{\circ}$ C in 10 years. As a result, snow cover forms later, it lasts shorter and water reserves in snow decline [6]. For these reasons, river runoff changes significantly. An analysis of river runoff change over the past decades has shown that spring floods are decreasing and winters are increasing, i.e. the redistribution of runoff between individual seasons is observed [7].

In order to provide scientific information on climate change and possible countermeasures on a global scale, the Intergovernmental Panel on Climate Change (IPCC) was established in 1988. The IPCC produces reports covering scientific, technical and socio-economic information on the risks of anthropogenic climate change and provides both

adaptation and mitigation measures. Five reports were produced in 1990, 1995, 2001, 2007, 2013 and the sixth report is currently under preparation.

For the first time, the IPCC's **First Assessment Report** (FAR) identified anthropogenic activity as increasing greenhouse gas concentrations, leading to global warming. In order to model future climate projections, 4 scenarios of SA90 Group (A, B, C, D) were developed to assess the consequences through a variety of impact measures. According to these scenarios, the air temperature will rise from 0.3 °C (A) to 0.1 °C (C) in a decade. FAR report used three-dimensional mathematical models of climate system general circulation (atmosphere-ocean-glacier-earth), which did not estimate greenhouse gas feedback, horizontal resolution was ~ 500 km [8].

The IPCC's **Second Assessment Report** (SAR) assessed population growth, political and economic developments in the former Soviet Union, Eastern Europe and the Middle East [9]. In climate modelling, six newly developed IS92 group scenarios (IS92a, IS92b, IS92c, IS92d, IS92e, IS92f) were used as input data and for the first time the full greenhouse gas composition was evaluated [10]. The SAR report used improved climate models with a horizontal resolution of ~ 250 km and atmospheric aerosols models were included [11].

**The IPCC's Third Assessment Report** (TAR) used SRES (Special Report on Emissions Scenarios) emission scenarios, which enabled to assess the climate and environmental consequences of GHG emissions as well as mitigation and adaptation strategies [10], although the measures themselves were not included. TAR used advanced AOGCM climate models supplemented by dynamical vegetation and carbon cycle models. Improved horizontal grid resolution of model was up to ~ 180 km [12].

Future climate projections of the IPCC's **Fourth Assessment Report** (AR4) were based on SRES emission scenarios and CMIP3 modelling (Coupled Model Intercomparison Project3) [13]. The first Earth System Model (ESM) was used with AOGCM models. Some climate models had a horizontal grid resolution of 50 km [14].

The IPCC's **Fifth Assessment Report** (AR5) was based on CMIP5 Coupled Model Intercomparison Project. New Representative Concentration Pathways (RCP) scenarios were created [13], based on the likely perspectives of humanity's economic and social development in order to assess the effects of climate change mitigation and adaptation. New emission scenario RCP2.6 was introduced integrating mitigation and adaptation measures in order to maintain average surface temperatures below 2 °C of pre-industrial levels [15]. The extent of land use intensity and changes in land cover were assessed [15], climate models were supplemented with features of biogeochemical cycles (carbon, sulphur), ozone change processes, atmospheric chemistry and continental glacial model [16]. The CMIP5 project carried out simulations with 50 GCM models having a horizontal spatial resolution of 50 - 300 km [17]. The IPCC continually encourages the scientific community to develop new scenarios that are consistent with scientific advances, up-to-date data, and supports the development of more integrated climate models [18].

In hydrology, hydrological models let us numerically model natural systems and solve various tasks. Hydrological modelling was introduced in the second half of the 19th century designing urban wastewater, land reclamation systems and hydro construction objects. For the water quality analysis [19], a mathematical model of mathematical description of the decomposition processes of organic matter in the river bed was introduced. In the EU, the models used in for hydrological modelling can be divided into two main groups: deterministic and statistical. Deterministic models are based on the study and evaluation of physical phenomena, whereas statistical models rely on the analysis of measured data of a phenomenon, completely ignoring its physical nature.

Hydrological modelling introduces methods of statistical analysis and, with the advent of computers, digital methods, allowing the greater use of methods based on physical processes.

The US Environmental Protection Agency developed QUAL, WASP, BASINS [20] and other models, and the Danish Institute of Hydrology produced MIKE models [21] used in hydrological modelling.

In the 21st century, mathematical models were applied for modelling of water runoff in Lithuania [22], [23]. The water balance model WATBAL was used to study changes in the Lithuanian water balance due to climate change [24]. The SIMGRO model was used to model the Dovine River [25]. The SIMGRO model was used for the investigations of the Dovine River basin [26]. The MIKE 21 NSW model was used to study wave energy resources in the Lithuanian coastal area of the Baltic Sea [27].

The HBV model was used to simulate runoff in Lithuanian rivers [28], [29], [30].

The application of various hydrological models offers wide possibilities for projection of hydrological characteristics using the output of climate models. Runoff predictions can provide guidance to the public on how to adapt to climate change. This paper begins a continued study, the first stage of which is the preparation of regional climate model data for the prediction of Lithuanian river runoff in future. This data will be used to assess the change in kinetic and potential energy resources of Lithuanian rivers in the 21st century and provide recommendations on how to more efficiently exploit river runoff for energy generation without harming the environment.

Research aim – adaptation of regional climate models output data (air temperature and precipitation) under RCP scenarios in the territory of selected Lithuanian rivers catchments for the period of 1986-2005 applying of Quantile Mapping method. The analysis of these data changes is done for the periods of near (2021-2040) and far (2081-2100) future.

# DATA AND METHODOLOGY

# Initial data

For the purposes of this study, daily air temperature (T,  $^{\circ}$ C) and precipitation (P, mm) data from 16 meteorological stations in Lithuania for the period of 1986-2005 were used (Fig. 1).



Fig. 1. Location of Lithuanian meteorological stations

The regional climate models ICHEC-EC-EARTH, MOHC-HadGEM2-ES, MPI-M-MPI-ESM-LR were extracted from the EURO-CORDEX database.

Air temperature and precipitation forecasts were prepared using 3 Representative Concentration Pathway scenarios: RCP2.6 – optimistic, RCP4.5 – moderate, RCP8.5 – pessimistic. Using the IMAGE model, the RCP2.6 scenario was developed, whereby

anthropogenic radiative forcing would reach 3 W /  $m^2$  in the mid-21st century and then begin to decline [31], [32]. For modelling the RCP4.5 scenario using the GCAM model, anthropogenic radiative forcing rises to 2100 and stabilizes at ~ 4.5 W /  $m^2$  [33], [34]. For modelling of RCP8.5 scenario using MESSAGE model, anthropogenic radiative forcing in 2100 exceeds the level of 8.5 W /  $m^2$  and continues to rise [35], [36].

#### **Data preparation for simulation**

Downscaling is used when the projected meteorological parameters (in our case T and P) need to be moved from the grid points of the climate model to the locations of specific meteorological stations. In 1997 Rummukainen list statistical, stochastic, dynamical and composite resolution enhancement methods [37]. Resolution enhancement methods are divided into dynamical and statistical ones. Dynamical downscaling is a computationally intensive process, usually performed in specialized climate research centres by assimilating global climate model data with regionally relevant parameters such as terrestrial and marine contrast, vegetation cover, etc. [38]. **Statistical downscaling** is a two-step process that identifies statistical relationships between finer-scale local climate variables and large-scale predictors, and then these relationships are used in large-scale results to model local climate characteristics in the future [38], [39]. This study used a statistical resolution enhancement method based on quantile mapping. Quantile mapping eliminates systematic errors in climate model data [40]. Calculations were made using the following equation [41], [39]:

$$St^{Obs} = h(St^{CM RP}) = ECDF^{OBS-1}(ECDF^{CM RP}(St^{CM Fut})), \quad (1)$$

where  $St^{Obs}$  – observed meteorological parameter,  $St^{CM RP}$  – climate model output for the reference period,  $ECDF^{Obs}$  – empirical cumulative distribution function for the observation period,  $ECDF^{CM RP}$  – empirical cumulative distribution function for climate model reference period,  $St^{CM Fut}$  – meteorological parameter, which is simulated by climate model for the future period. All calculated results are assessed with respect to the reference period (1986–2005).

#### RESULTS

In order to avoid extreme values of precipitation and air temperature and to obtain more accurate results, we analysed the average output of ICHEC-EC-EARTH, MOHC-HadGEM2-ES and MPI-M-MPI-ESM-LR climate models. Precipitation deviations (%) from the projected reference period (1986–2005) of these three models are presented in Fig. 2.



Fig. 2. Distribution of projected average seasonal precipitation in Lithuania (in % comparing projections of 2021–2040 and 2081–2100 with the average values of 1986–2005)

The projections show that precipitation is expected to increase in the near future. The average annual rainfall for RCP2.6 will increase by 2.9%, for RCP4.5 by 10.0% and for RCP8.5 by 8.8% compared to the reference period. Even greater changes in precipitation are expected in the far future. The average annual rainfall under RCP scenario 2.6 is projected to increase by 5.3%, under RCP4.5 by 9.1% and under RCP8.5 scenario by 22.9% compared to the reference period. Evaluating the seasonal nature of precipitation changes, it was found that the greatest increase in precipitation will occur in spring and winter, both in the near and far future. Winter rainfall will increase the least, and in the near future, according to RCP2.6 scenario, summer rainfall may decline by 5.4%.



Fig. 3. Distribution of projected average seasonal air temperature in Lithuania (in °C comparing projections of 2021–2040 and 2081–2100 with the average values of 1986–2005)

Air temperature deviations (°C) from the reference period in the near and far future are shown in Fig. 3. The air temperature is expected to rise in the near future. The average annual air temperature under RCP2.6 scenario will increase by 1.1 °C, under RCP4.5 - 1.3 °C and under RCP8.5 scenario by 1.4 °C compared to the reference period. Even greater changes in air temperature are possible in the distant future. The exception is the RCP2.6 scenario, according to which the air temperature will stop rising and stabilize. However, according to RCP4.5 and RCP8.5 scenarios, the air temperature is going to increase by 2.4 °C and 4.6 °C, respectively, if compared to the values of the reference period. The analysis of air temperature changes in different seasons has shown that in the near and far future the greatest changes are projected in winter, the moderate - in spring and autumn, and the smallest – in summer.

# CONCLUSIONS

- In the near future, precipitation is expected to increase. Average annual precipitation in the near future will increase from 2.9% (RCP2.6) to 10.0% (RCP4.5) compared to the reference period. In the long term, these changes will be even more significant, with annual average precipitation by 5.3% (RCP2.6) - 22.9% (RCP8.5) greater than during the reference period. Evaluating the seasonal nature of precipitation changes, it was found that the largest increase in precipitation will occur in spring and winter during the both future periods. Winter precipitation will increase the least, whereas in the near future, according to RCP2.6 scenario, summer precipitation may decline by 5.4%.
- 2. The projection showed that the average annual air temperature is going to increase over the periods of 2021-2040 and 2081-2100 compared to the reference period of 1986-2005. In the near future the air temperature will be from 1.1 °C to 1.4 °C and in the far future from 1.3 °C to 4.6 °C higher than in the baseline. In both periods, the smallest changes are predicted by RCP2.6 scenario and the largest changes by RCP8.5 scenario. The analysis of the changes in air temperature in different seasons showed that in the near and far future the greatest changes are projected in winter, the moderate in spring and autumn, and the smallest in summer.
- 3. The performed projections of precipitation and air temperature in the near and far future allow to conclude that the expected changes may have significant influence on the distribution of Lithuanian river runoff during the year and thus on the seasonal availability of hydroenergy resources.

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# ANALYSIS OF THE USE OF WOOD TO MITIGATE CLIMATE CHANGE AND PROMOTE THE BIOECONOMY IN LITHUANIA

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#### ABSTRACT

Climate change is having a negative impact on ecosystems and threatening humanity. In order to mitigate this effect, many countries in the world have the United Nations Framework Convention on Climate Change In the process of implementing the Convention, they are committed to reducing greenhouse gases emissions and/or increase absorption. In implementing the Paris Agreement on Climate Change, each party to the agreement chooses national climate change mitigation measure in individual sectors. The forestry sector, including timber products, makes a significant contribution to climate change mitigation. Forests absorb carbon dioxide from the atmosphere and store it carbon in biomass, soil, and some deforestation can be conserved after deforestation in wood products. Increasing carbon stocks in wood products is United Nations recognized tool for climate change mitigation. The Intergovernmental Panel on Climate Change is developing guidelines that set out the differences carbon accounting methods for wood products. Depending on the available data on wood products, Member States may choose the method. Wood flow analysis is consistent the highest carbon accounting method, where annual carbon receipts are accounted for, using country-specific data. The main purpose of this work is to analyse the industrial wood flows in Lithuania and to determine carbon stocks and their quantitative changes in wood products. To achieve this goal, a survey of wood processors was conducted in Lithuania, which covered over 50% of the total raw wood produced in the country. The results of this work can be used not only for carbon accounting of wood products. Wood flow analysis can be useful in analysing wood processing sector in Lithuania and in making decisions on the use of wood. It is recommended that such analyses in Lithuania would be performed periodically. From the collected primary data, we can see that a significant part of wood in Lithuania is used as sawn timber, which allows coal to be locked for up to 35 years. However, at this point, we can significantly increase the consumption of sawn logs in the construction sector by replacing iron and concrete structures, thus locking up even more carbon in wood.

Keywords: climate change, forest, carbon absorbing, carbon cycle, bioeconomy

#### **INTRODUCTION**

Numerous studies note that climate change is having a negative impact on all ecosystems as well as the extreme effects of climate change such as hurricanes, ocean acidification, other forms of extinction, droughts and heat waves, bus frequency and intensity (IPCC,2014). For climate change mitigation, back in 1992. the United Nations Framework Convention on Climate Change was approved. The last important decision, still in the "Paris Agreement", setting a long-term goal, limit climate warming to 2 ° C by the end of this century (United Nations, 2015). The parties to the agreement, including Lithuania, increase their capacity to adapt to the negative effects of climate change and lower greenhouse gas (GHG) emissions. To achieve this long-term goal, each party to the agreement must act at the national level, which has climate change mitigation measures in place to reduce GHG emissions nationwide and adapt to the effects of climate change (United Nations, 2015). In implementing the framework agreement, the parties must reduce gas emissions and/or increase absorbers by removing gas. This means that countries must actively exploit the potential for climate change mitigation, including by increasing carbon stocks in forests. Many of the national climate change mitigation measures presented focus on the forestry and forestry sector (Pilli et. Al.,

2017). Forests, by absorbing carbon from the atmosphere, have a major impact on the global carbon cycle. During photosynthesis, forests absorb CO2 from the atmosphere and store carbon in biomass. Some of the carbon stored in the forest remains in timber products after felling, which is why carbon storage and storage in the forestry sector is recognized as a global strategy to support climate change mitigation measures (Chen et al., 2010).

In Lithuania in 2010-2017. over 20.6 million tonnes were emitted into the atmosphere on average tons of CO2 eq. (EUROSTAT, 2020). 2017 the energy sector was the most significant source of GHG emissions, accounting for 55.5% of total emissions. Other polluting sectors in terms of GHG emissions in Lithuania were agriculture - 21.5%, industry 17.8% and the waste sector 5.1% of total emissions. However in 2017 the land use, land use change and forestry sectors absorbed over 26% of all GHG emissions in that year (NIA, 2019), while forest land and timber products in 2017. absorbed -9 mln. tons of CO2 (Figure 1), almost half of the emissions that year. This means that the forestry sector in Lithuania is extremely important in mitigating climate change. Lithuania could make more active use of climate mitigation potential by improving carbon accounting methods and increasing carbon stocks in the forestry sector.

**The aim.** Thus, the aim of the study is to determine the carbon stocks in harvested wood products and their quantitative changes in the changing economic conditions in Lithuania.



Fig. 1 CO2 emissions and absorption in Lithuania 1990 - 2017 in the land use, land use change and forestry sectors (according to NIA, 2019).

# METHODOLOGY

# To identify the main buyers of raw wood and to find out the quantities of wood purchased, exported and imported in Lithuania, as well as the assortment structure in 2017 period

To implement this task, data was collected on the buyers of raw timber sold and the quantities purchased by them from the State Forest Enterprise and the BALTPOOL timber exchange in 2017-2020. After receiving the data on the buyers, they were be surveyed – how many and what assortment structure of raw wood or wood products semi-finished products

were used in the production process (Table 1). In total, more than 100 companies was surveyed. An analysis of the data obtained will be performed later.

# Table 1. Quantities of raw wood purchased by Lithuanian wood processors.

# Company name:

20... quantities of raw wood and wood products used

How many and what kind of wood products 20 ... were used in your company for the production of wood products. If several round wood assortments or wood products (eg sawn logs, paperwood, firewood, semi-finished products, chips, sawdust, deforestation waste, etc.) have been used in the production process, please indicate their quantities separately. Be sure to specify units of measurement (m<sup>3</sup>, tons)

Product name	Quantity j in Litl	purchased nuania	Imported quantity					
		20	20	•	20			
	20		Quantity	From which state	Quantity	From which state		

# To identify the main buyers of raw wood and to find out the quantities of wood purchased, exported and imported in Lithuania, as well as the assortment structure in 2017-2020 period

To implement this task, a survey was prepared and sent to Lithuanian wood product producers / processors and exporters to find out the use of wood in primary production processes and their sale in the local market, as well as exports (Table 2). Manufacturers of wood products will also be asked to indicate the shelf life of their products, taking into account the technical characteristics of the products.

Table 2. Harvested wood products (HWP) produced by Lithuanian wood processors and their sale.

How many and what kind of wood products 20 .. has been produced in your company (eg construction wood, particle board, paper, briquettes, pellets, etc.). If several wood products have been produced, please indicate their quantities separately. Be sure to specify units of measurement (m<sup>3</sup>, tons)

Product name	Quantity sold in Lithuania	Quantity exported	Depending on the technical characteristics of the products, please estimate the average service life of the product (etc., 5, 10, 20, 30100 years)
Construction timber			
Chipboard			
Paper			
Briquettes			
Pellets			
Other			

#### To calculate carbon stocks and their change by HWP second and third stage methods

#### Accounting methodology for carbon stocks and their change (Tier 2 method)

The equations below was used to calculate carbon stocks and their change in HWP as specified in the IPCC guidelines. In particular, the ratio of HWP produced from domestically produced raw wood will be calculated. Subsequently, the annual receipts are multiplied by the carbon coefficients (Table 3). Finally, the annual change in carbon stocks will be calculated.

Equation (1) to calculate the ratio of domestically produced sawn timber to wood-based panels from domestically produced raw timber (IPCC, 2014, Equation 2.8.1):

$$f_{IRW}(i) = \frac{IRW_{P}(i) - IRW_{EX}(i)}{IRW_{P}(i) + IRW_{(IM)}(I) - IRW_{EX}(i)} , (1)$$

where

 $f_{IRW}(I)$  = domestic HWP to create a share of the consumption of roundwood from local forests per year *i*;

 $IRW_{P}(i) =$  production of round industrial wood, excluding wood from deforestation sites, per year *i*, *Gg C metai*<sup>-1</sup>;

 $IRW_{EX}(i) =$  exports of industrial roundwood per year *i*, *Gg C years*<sup>-1</sup>;

 $IRW_{(IM)}(I)$  = imports of industrial roundwood per year *i*, *Gg C* years <sup>-1</sup>;

Equation (2) to calculate the ratio of domestically produced paper products to domestically produced wood pulp (IPCC, 2014, Equation 2.8.2):

$$f_{PULP}(i) = \frac{PULP_{P}(i) - PULP_{EX}(i)}{PULP_{P}(i) + PULP_{IM}(i) - PULP_{EX}(i)} , (2)$$

 $f_{PULP}(i)$  = The share of domestically produced wood pulp is used for the production of paper and board domestically per year *i*.

PULP<sub>P</sub>(*i*) = wood pulp produced per year *i*, *Gg C years* <sup>-1</sup>; PULP<sub>IM</sub>(*i*) = wood pulp imported per year *i*, *Gg C years* <sup>-1</sup>; PULP<sub>EX</sub>(*i*) = wood pulp exported per year *i*, *Gg C years* <sup>-1</sup>.

Table 3.	Coefficients	set jointly	for	countries to	calculate	the	carbon	ratio	HWP	(TKKK
				0011						

2014).								
HWP category	Density Mg m <sup>-3</sup>	C conversion factor (by dry air						
		mass), C m <sup>-3</sup>						
Sawn timber - coniferous	0,450	0,225						
Sawn timber - deciduous	0,560	0,280						
Shell	0,505	0,253						
Glued plywood	0,542	0,267						
Dust plate	0,596	0,269						
Wood fiber board	0,788	0,335						
MDF	0,691	0,295						
Extruded Fibro board	0,739	0,315						
Insulation board	0,159	0,075						
_	dry wood pulp Mg Mg <sup>-1</sup>	by dry air mass, Mg C Mg <sup>-1</sup>						
Paper and board (total)	0,900	0,386						
### Data flow analysis methodology (Tier 3 method)

The Tier 2 method accounts for coal in HWP produced only from round raw wood, but in reality the production of HWP, such as wood panels or paper, and from secondary raw materials such as sawdust, wood chips, waste paper. Using data flow analysis, it is possible to trace wood (coal) in the forest sector (Binder et al. 2004; Korhonen et al. 2001). Wood flow analysis is an important element in estimating current carbon inflows (Jasinevičius et al., 2015). In this work, carbon stocks and their change will be calculated according to the Tier 3 method. The data used will be obtained from the data (carbon) flow analysis. The data collected from the prepared questionnaire will be used in this work.

To obtain the data, a survey of wood companies will be conducted to find out exactly what wood is used in the production of HWP semi-finished products and to estimate the half-life values of the products. The wood value chain is based on the carbon calculation principles set out in the United Nations Decision (2 / CMP.7, 2012) described in the analysis of this report. Imported timber and timber from deforestation are excluded from the timber accounting chain in the data flow analysis.

According to the IPCC guidelines, the Tier 3 approach must cover at least three main categories of HWP (sawn timber, wood-based panels, paper and board). In this work, five groups of HWP will be analysed (Table 4).

HWP category	Source	Half value (years)	Coal revenue share (%)
"Wood panels"	IPCC	25	
Sawn timber	IPCC	35	
Short-term sawn timber	Calculated in this work		
(Euro pallets)	Calculated in this		
	work		
Glued beam (CLT)	IPCC	2	

Table 4	The 3-ster	n method uses	country-specific	and country-	specific half-lives
1 auto = 1	THE J-SIC	J memou uses	country-specific	and country -	specific nan-nyes

In summary, the method described above is consistent with acceptable carbon calculation principles and meets the requirements of the Tier 3 method. In order to compare the results of the different methods, carbon stocks and their changes will be calculated according to the Tier 2 and Tier 3 methods.

The conversion factors to carbon used in the Tier 3 method to determine the carbon fraction of HWP are given in Table 5.

Table 5. The carbon to carbon conversion factors used in the Tier 3 method are used to determine the carbon fraction of the HWP. The carbon content of any species is 0.5. The conversion factors set out in the IPCC are used to calculate the carbon content of the Tier 2 method

method.						
Туре	Weight kg / m3 (dry	Carbon fraction kg /	<b>Conversion factor</b>			
	wood)	m3				
Pine	520	260	0.26			
Spruce	450	225	0.23			
Birch	650	325	0.33			
Aspen	510	255	0.26			
Black alder	540	270	0.27			
White alder	490	245	0.25			
Oak	760	380	0.38			
Ash	750	375	0.38			

Source: Order of the Minister of the Republic of Lithuania, 2002: "Measurement of round wood and uncut forest and rules for determination of wood values".

# RESULTS

## Analysis of wood flows in Lithuania, determination of carbon stocks and their change

During the survey of wood processors, data were obtained from 72 wood companies operating in Lithuania and producing primary wood products. The main focus was on companies processing the largest quantities of raw wood, but small and medium-sized enterprises were also surveyed. Data were collected for all categories of NMPs analyzed in this work. The analysis of the submitted data covered 3758 thousand. m3 of local wood flows. This represents 54% of the total in 2017. In Lithuania, raw timber is prepared by main and intermediate felling. In order to perform a nationwide analysis of timber flows, statistical data of the State Forest Service on raw timber production in Lithuania were used.

The results of the study revealed that in 2017. The amount of raw wood prepared by main and intermediate felling in Lithuania was 7000 thousand. m3. 1899 thousand m3 of this timber was exported, and 1403 thousand. m3 was used for energy production, therefore 3699 thousand m3 was used for primary NPPs. m3 of domestically produced raw wood: 2959 thous. m3 of sawn logs, 214 thous. m3 of paper trees, 258 thous. m3 of wood panels and 268 thousand. m3 of firewood. The largest part of sawn logs – 1976 thousand. m3 was used for the production of sawn timber, of which 996 thousand were produced. m<sup>3</sup> of sawn timber. 688 thousand tons were used for the production of EURO pallets. m<sup>3</sup> of sawn logs, of which 363 thousand were produced. m<sup>3</sup> of pallet blanks. 202 thousand was used for the production of particle board. m<sup>3</sup> of paper trees, 258 thous. m<sup>3</sup> of panel wood, 268 thous. m<sup>3</sup> of firewood and 327 thousand. m<sup>3</sup> of wood waste (chips and sawdust), of which 838 thous. m<sup>3</sup> of plates. 185 thousand was used for the production of glued plywood and veneer. m3 of sawn logs and 11 thousand. m3 of paper trees, of which 79 thousand. m<sup>3</sup> of glued plywood and veneer. 110 thousand was used for the production of glued beam and log blanks of sawn logs, of which 23 thousand. m<sup>3</sup> of glued beam and 35 thousand. m<sup>3</sup> of log blanks. During the production, 1541 thousand. m<sup>3</sup> of various wood waste, some of which was used in the production of particle board, the remaining waste was exported or used for energy production (Table 6).

HWP category	Import wood	Quantity imported (thousand. m <sup>3</sup> )	Share of imported wood in production (%)	Imported from the country
Sawn timber	Saw logs	125	6	Poland
Sawn timber (EURO pallets)	Saw logs	97	12,5	Poland,
				Latvia
Particle board	Shavings,	72	6,4	Belarus,
	sawdust			Poland
Glued plywood and veneer	Saw logs	11	5,3	Latvia
Glued beam and blanks for the	Saw logs	8	7	Poland,
construction of log houses				Latvia
Total imported	31	13 thousand. m <sup>3</sup>		

Table 6. Volume of raw	wood and wood	waste imported to	o Lithuania	(2017).
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## Analysis of exported wood

Preliminary analysis of exported timber revealed that in 2017. 1899 thousand tons were exported from Lithuania. m3 of raw wood. Most of the pulpwood were exported – 912 thousand. m<sup>3</sup>, 684 thousand tons of sawn logs were exported. m<sup>3</sup>, plywood – 167 thousand. m<sup>3</sup> and firewood – 136 thousand. m<sup>3</sup>. Most of the raw wood was exported to Latvia, Poland and Sweden (Table 7).

Assortment / Importing country	Latvia	Poland	Sweden	Germany	Finland	China	Other*
Saw logs	439	87	59	67	-	18	14
Pulpwood	260	232	293	-	115	-	12
Panel wood	117	50	-	-	-	-	-
Firewood	82	54	-	-	-	-	-
Total	898	423	352	67	115	18	26

Table 7. Quantities of exported timber by ranges and importing countries.

\* Insignificant quantities of timber exported to other countries are classified as "Other".

Table 8. Distributio	n of processing	of raw woo	d produced in	Lithuania into	wood products in
other countries.					

Importing	La	tvia	Po	land	Sw	veden	Ger	many	Fi	nland	Cl	nina
Country / Use	Ratio of use of sawn logs in other countries (FAO data) and possible use of sawn											
-	logs e	logs exported from Lithuania										
	%	tūk.m <sup>3</sup>	%	tūk.m <sup>3</sup>	%	tūk.m <sup>3</sup>	%	tūk.m <sup>3</sup>	%	tūk.m <sup>3</sup>	%	tūk.m <sup>3</sup>
For sawn	02 4	405.4	80.2	77.6	00.3	58.6	00.2	66 5			12.5	77
wood	92,.4	403.4	09.2	77.0	99.5	58,0	99,2	00,5		-	42.3	7.7
For the shell			1.1	1.0	0.2	0.1	0.4	0.3		-	1.5	0.3
Plywood	7.6	33.6	9.7	8.4	0.5	0.3	0.4	0.3		-	56.0	10.1
		Pos	sible ı	use of ot	her rai	nges exp	orted fr	om Lithu	iania	thous.	m3	
For paper products		-	2	.32	2	480		-		188		-
Particle board	1	17		50		-		-		-		-
Energy	8	32		54		-		-		-		-

# CONCLUSION

Evaluating the essential and other results of the research, it can be concluded that:

- The analysis of wood flow in Lithuania revealed the flows of industrial wood use for the production of primary wood products. This analysis is in line with the tier three carbon accounting approach set out in the IPCC guidelines, where annual carbon revenues are accounted for using country-specific data.

- The analysis of timber flow clearly distinguishes between imported and exported raw timber flows in Lithuania, but a more detailed analysis of the use of exported raw timber in other countries would require additional data on the use of this timber. The survey of raw timber exporters is not sufficient, as in most cases the answers are based on assumptions.

- The results of this work can be used not only for carbon accounting in wood products. Wood flow analysis can be useful in analysing the wood processing sector in Lithuania and in making decisions on wood use.

- It is recommended that such analyses be performed periodically in Lithuania, as this would enable the analysis of wood use trends and carbon accounting in wood products, applying the top-tier method.

In the future, the systematization of all collected data will allow a more accurate calculation of carbon stocks in different harvested wood products, as well as a deeper analysis of how long carbon is locked in each harvested wood product and a comparison of carbon stocks using Tier 2 and Tier 3 methods.

However, we can already see that the largest consumption in Lithuania is sawn wood, which locks coal for the longest period of time. Therefore, in order for the timber industry to continue to make a significant contribution to reducing GHGs, it is necessary to maintain existing timber use capacity and to promote the sustainable production of as much good quality sawn timber as possible through sustainable forest management. Also promote the use of wood in the construction sector as a substitute for iron and concrete, which contribute to CO2 emissions.

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# METHODOLOGY FOR ASSESSING REUSE POTENTIAL AND SUSTAINABILITY IN REGION LEVEL

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#### ABSTRACT

In circular economy, prolonging product life cycle is one of the key ways to manage resources efficiently, which can be achieved through the reuse (R) and preparation for reuse (PR) of products.

In most EU Member States, R and PR at the public sector level are related to waste management, and only a few countries are developing successfully at the national or regional level.

The Alytus region was selected for the study as the only region in Lithuania where a PR center already exists and 20 item exchange points are located in each sorting center.

Based on the municipal waste material flows and WRAP reuse tool, the R potential and its sustainability in the Alytus region, as a waste management activity, were assessed. The results of the assessment showed that reuse and preparation for reuse (RPR) could be one of the main effective resource management activities and could be implemented in all sustainability aspects.

In the Alytus region, based on the current PR volume (76 t in 2020) and applying the Belgian experience scenario (2), 1,163 t of waste could be PR by the year 2039, i.e., the volume of waste disposed by landfilling would go down by 2.7 percent (476 t) and up to 1.6 percent of waste could be taken back for R. Meanwhile, according to the Bavarian (Germany) experience scenario (1), by the year 2043, the amount of waste ending up at landfills would go down by 7.8 percent (1,347 t), and the overall PR flow (3,370 t) would make up around 5.2 percent of the waste managed at waste management facilities of the Alytus region (in 2020, 72,108 t was handled).

The higher financial costs incurred during PR activities can be reduced by promoting direct R, for example, through mutual exchange, online sales, donations to charities (e.g., PR of 1 t of furniture – EUR 405 and R – EUR 6.16); therefore, it is useful for waste management organizations to consider PR as one of the measures to promote waste prevention.

Considering the social aspect, in Scenario 1 and Scenario, 2 PR creates more jobs compared to the waste management activities performed instead of PR (recycling and disposal). However, this indicator may decrease or increase depending on the type of waste PR and the type and proportion of waste management methods (recycling, landfilling or incineration) used prior to the PR activities.

\* The article has been prepared on the basis of a master's thesis [35].

**Keywords:** reuse, preparation for reuse, circular economy, efficient resource management, sustainability, environmental impact, economic impact, social impact, Alytus region

#### **INTRODUCTION**

The EU Sustainable Development Strategy (COM(2005) 658 final) [1] addresses the global objectives and principles of sustainable development, and one of the core steps in implementing this strategy is transitioning to the circular economy (CE), enshrined in a number of legal acts.

The latest European Commission (EC) communication on sustainable development and transitioning to the CE in the EU – the European Green Deal (COM(2019) 640 final) [2] – sets out a new growth strategy, one of the main goals of which is to completely reduce net greenhouse gas (GHG) emissions and decouple economic growth from resource use through efficient management, which is planned to be put into practice through the "Mobilizing industry for a clean and circular economy" element. It is planned to focus on resource-intensive sectors such as textiles, construction, electronics and plastics.

The main goal of the EU CE Action Plan [3], based on the communication titled the European Green Deal, is to shift to the CE with a longer value retention of products, materials and resources in the economy and, as far as possible, minimized waste volume, meaning that by giving priority to the volume reduction and reuse (R) of materials before recycling, it is sought to strengthen and extend the responsibility of manufacturers, to provide measures to encourage companies to offer reusable, durable and repairable products and to create conditions enabling consumers to choose them.

Other significant and relevant documents related to effective resource management are the Directive 2008/98/EC on waste [4] and the revised Directive 2018/851 on waste [5].

The Directive 2008/98/EC [4] considers the waste hierarchy as the main waste policy principle in EU Member States, according to which the highest priority is given to waste prevention and preparation for reuse (PR). To promote priority waste management methods, EU Member States are required to take up measures encouraging product reuse and preparation for reuse (RPR) by, first and foremost, setting up and promoting R and repair networks.

The revised Directive 2018/851 [5] foresees municipal waste R and recycling targets: by 2025 - 55 percent, by 2030 - 60 percent and by 2035 - 65 percent. As one of waste prevention measures, it is envisaged to encourage product R and develop repair and R promotion systems, giving priority to electrical and electronic equipment, textiles, furniture, packaging, construction materials and products and to set appropriate quantitative and qualitative indicators and objectives first and foremost related to the quantity of waste generated.

Therefore, waste management tasks and accountability for waste prevention set for EU Member States as well as the consideration of effective resource management as one of the most significant measures to transition to the CE led to the fact that not only private initiatives and business enterprises, but also national, regional or local institutions started RPR activities. R and recycling centers (urban resource centers) [6] are considered to be among the effective resource management measures at the local (city, region) level. These centers may be established by municipalities, private businesses or act as charitable organizations [7].

In literature, RPR is often referred to as R; however, one difference between the concepts can be pointed out (2008/98/EC) [4]: PR is related to waste management (equipment, collection procedures and tools), while R is an element of waste prevention, aimed at consumption (operational activities) and not at the processes of preparation for further use applied in PR.

Gusmerotti et al. [10] consider R as giving products away or selling them in a secondhand market (e.g., various ad portals or social network groups) because then the waste is immediately reduced, regardless of the operations required for further R. When the same type of product is delivered to the waste collection system, it can also be used again but only after performing a few operations, in line with the requirements of the waste management system, and the author considers this case as PR. According to Gharfalkar et al. [15], PR is waste management and covers inspection, cleaning, safety and functionality inspection and repair operations. Products, PR according to selected activity models, are distributed in a chosen way – sold directly to final consumers, suppliers or resellers [38].

Geissdoerfer et al. argue R is one of the paramount activities in implementing the CE [10].

Singh and Ordoñez [11] believe manufacturing-centered take-back systems are the most efficient method of R, disassembling and renewing, which are inefficient in practice, and the collection of products of parts thereof is conducted through waste management. For this reason, the author proposes to exploit the potential of the R waste management system to the maximum extent for the efficient and closed-loop resource use, which might serve as a basis of future product collection systems.

Parajuly and Wenzel [12] argue a waste management system can help create value from a discarded product, but its PR requires an efficient collection system.

According to a study by Kissling et al. [13], in the waste management sector, products/items or parts thereof that entered the waste management system (through sorting centers, waste collection rounds, special campaigns or other ways chosen by the organization responsible for waste management) are managed as waste. Usually, local government institutions perform product collection and sorting for R, and for-profit and non-profit organizations conduct PR.

Zeleny M. [16] classifies RPR activity models/systems according to the type of ownership: private charitable and non-profit centers operating as social enterprises that aim to provide people with an opportunity to reintegrate into society or have other social objectives; private centers that mainly focus on profit and further operation; subsidized organizations, established as part of the infrastructure of municipal-level waste management companies that focus on preventing waste.

Products/waste flows, relevant for RPR, can be identified in accordance with the municipal waste definition laid out in the revised Directive 2018/851 [5]: "<...> mixed waste and separately collected waste from households, including paper and cardboard, glass, metals, plastics, bio-waste, wood, textiles, packaging, waste electrical and electronic equipment (WEEE), waste batteries and accumulators and bulky waste, including mattresses and furniture <...>." In addition, the relevant products/waste flows can be identified in relation to the priority product/waste flows (i.e., WEEE, batteries and vehicles, packaging, plastics, textiles, buildings and construction, food products and nutrients) set out in the latest CE Action Plan [3].

Messmann, L. et al. [14] conducted a study analysing the RPR potential of items collected in sorting centrers (Bavaria, Germany), focusing on WEEE, furniture and leisure products.

Zacho, K. et al. [17] conducted an analysis of the PR and recycling of waste in Denmark's municipalities, revealing that more than 3 percent (excluding WEEE) of municipal waste, such as books, clothing, textiles, glass jars, porcelain, ceramics, furniture, construction materials and bicycles, is suitable for RPR.

Gusmerotti, N. et al. [10] analysed the PR generally and highlighted bicycles, furniture and WEEE as examples of items that can be managed in this way.

According to legislation and the aforementioned studies, RPR is best suitable for waste that was used as household items before becoming waste: WEEE, textiles, bulky and other (plastic, metal, glass, wood and paper) items.

Therefore, taking into account these aspects and the fact that efficient resource management and transitioning to the CE are a part of the EU Sustainable Development Strategy, which contributes to the implementation of the 2030 Agenda for Sustainable Development, it is useful to prepare a methodology for RPR activity potential assessment for organizations engaged in this activity, which would allow to assess the impact of product R and PR activities

on the change of material flows in the context of the CE in social, environmental and economic aspects.

## MATERIALS AND METHODS

In order to assess the RPR potential and sustainability of items, a complex methodology has been developed. The methodology covers the following:

1. Material flow analysis (MFA), using STAN [18], which helps assess the flow of items suitable for RPR, entering the waste management system in a certain territory (in this case, the Alytus region).

2. Application of the Product R Tool [19], developed by WRAP, when the economic, social and environmental impact analysis of the RPR activity is performed (when the social impact is perceived as job creation, the economic impact – as an economic benefit for households both in terms of selling unwanted items and purchasing them at a lower price and the environmental impact – as reducing GHG emissions) on the basis of the maximum possible quantity of RPR items identified during the MFA.

3. Summary of research findings and recommendations on RPR potential assessment applicable in a specific case.

## RESULTS

The Alytus region (Lithuania) was chosen for the application of the methodology and assessment of its efficiency. In the Alytus region, in one of the first municipal sorting centers in Lithuania, through an established company titled JSC Alytus Region Waste Management Center (ARWMC), not only 20 R (item exchange) points *Mainukas* but also an item RPR center *TikoTiks* were established in the end of 2019.

These two waste reduction activities complement each other and facilitate the development of RPR activities, integration of all sustainable development aspects and implementation of waste reduction at a regional level when these activities are carried out by the public sector through a waste management company established by the municipality. In this region, the official accounting of RPR items was started in the Q1 2020.

#### Material flow analysis

The MFA, with the help of STAN, is useful for the quantitative assessment of the maximum possible RPR potential of items, analysing waste management processes in the facilities constituting the municipal waste management system. According to the data of the Alytus Region Waste Management Report [20], 81,461 t of municipal waste was generated in the Alytus region in 2020, of which 17,102 t (21 percent) was disposed of by landfilling.

Based on the RPR item flows identified in the literature analysis (WEEE, textiles, bulky and other items (plastic, metal, glass, wood and paper)), the 2020 report of the ARWMC [20] and the MFA conducted, the scheme of material flows (import/export) of the Alytus region waste management system was created, and it was determined that RPR items come about during the sorting for recycling process, which takes place in 20 sorting centers. This is because various items and materials that do not fit or are not allowed to be disposed of in waste containers reach the sorting centers. In addition, item exchange points *Mainukas* are located at the sorting centers, and items to be repaired are transported from these centers to R center *TikoTiks*. In sorting centers, 55 percent of waste is recycled, and the remaining waste, which is

mostly constituted of the soft part left after furniture dismantling and insulation materials, is disposed of by landfilling.



Fig 1. Alytus region municipal waste MFA in 2020

In sorting centers, WEEE, textiles and furniture, which comprise the largest share of the bulky waste collected, are accounted for separately; meanwhile, various household items, children, leisure and other items are classified as secondary raw materials in terms of the predominant material: e.g., plastics – various plastic utensils, furniture; glass – window glass; metal – various metal utensils, metal frames for bicycles or other items; wood – picture frames, boards of various length, wood separated from construction and demolition waste; paper – books.

Summarizing the application of MFA in the Alytus region, theoretically RPR items come to light in sorting centers (green field in Figure 1). In the year 2020, 712 t of textile products, 542 t of WEEE, 4,625 t of furniture, 141 t of plastic products, 231 t of paper products, 389 t of glass products, 156 t of metal products and 185 t of small wood products was collected in the said centers, which means that in the Alytus region RPR items can take shape in 6,981 tons of waste.

#### Impact assessment of product reuse and preparation for reuse using WRAP tool

In the tool, the R of items is considered to be a direct R: used items are sold online, donated to charities, second-hand shops. The PR activities start when used items enter the waste management system (e.g., are delivered to sorting centers), as in the case of the Alytus region.

Based on the possible PR quantitative potential of the Alytus region, determined when performing the MFA, and using the WRAP tool [19], the environmental, economic and social impact of the PR activities was assessed, comparing it with the current item management methods and their impact on the environment.

For this assessment, it is necessary to investigate what part of the PR waste stream identified during the MFA (6,181 t) is eligible for PR only.

After analysing nationally applied or research-established quantitative PR targets/volumes for textile products [7], [22], [23], [24], [25], [26], WEEE [7], [12], [14], [27], [28], [29], furniture [7], [14], [25], [30] and other household items [14], [30], quantitative indicators of the overall municipal waste flow [6], [17] and per capita [7], the study on PR potential of items conducted in Bavaria, Germany [14], was chosen in order to determine the PR item share in the overall waste stream (6,981 t). Compared to others, this study is one of the most recent ones (2019), conducted in sorting centers and on a large scale (in the whole region), in as many as 60 sorting centers, and the majority of PR items come about in these centers in the region. According to the results of this study, between 13 percent and 16 percent of electrical and electronic equipment, furniture and leisure products delivered to the sorting centers are in excellent condition and can be easily PR. In addition, having implemented improvements in the collection, storage and management of this waste to prevent new damage to the items, their R potential could be increased by an additional 13-29 percent.

For a broader comparison and evaluation, the De Kringwinkel ViTeS R network in Flanders (Belgium), which has a quantitative R target set – to collect and transfer up to 7 kg of used items per capita by the year 2022 [7] – has been additionally selected. This network acts as a second-hand shop or collection point where the items are inspected and repaired before a sale/delivery, which is considered a direct R, as the extended life cycle of items prevents them from entering the waste management system, where the same or similar activities are already considered as PR.

This network has been operating for the longest time – since 1991 – and is one of the most successful examples of R activities.

In the Q1 2020, official accounting of PR items was introduced in the Alytus region, and this year about 76 t of items (13 t of textile products, 37 t of furniture, 12 t of WEEE and 14 t of other items) [20] was PR, which is considered as the current situation (Scenario 0) and compared with the other two scenarios (Scenario 1 and Scenario 2).

The quantitative volumes for Scenario 1 are based on the proportions of PR items [14] (Scenario 1) identified during the study in Bavaria, Germany, and are presented in Table 2. In this study, items suitable for R are considered to be products of good-quality delivered to sorting centers that do not require any repair operations. By the same token, items suitable for PR are considered to be items suitable for use but having minimal or medium defects.

In this case, the PR potential of textiles is estimated based on the Estonian experience, where 14 percent of the textiles is R within the country [31]. This path was chosen because the study in Bavaria [14] did not examine the PR potential of textile products that had entered into the waste management system.

Table 1. I scenario: RPR potential of Alytus region based on the results of a study in Bavaria, Germany [14]

1 scenario	During MFA identified flows to estimate Alytus region RPR	According research [14] det (%) from the total amou sorting centers (excluding to possible amount of RPR in R		Possible amount of RPR in Alvtus		
	quantitative potential, t	%	t	%	t	region, t
Textile	712	0%	0	14%	100	100
WEE	542	19%	103	39%	211	314
Furniture	4625	12%	555	43%	1989	2544
Plastic	141					
Paper	231					
Glass	389	31%	342	39%	430	772
Metals	156					
Wood	185					
Totl:	6981	1100			2630	3730

According to the PR proportions determined in the study [14], in case of Scenario 1, it is possible to PR 3,730 t of waste in the Alytus region.

The possible quantitative potential of the Alytus region in Scenario 2 is based on the quantitative target of the study in Flanders, Belgium [7], and calculated on the basis of the population of the Alytus region in 2020 (166,135 inhabitants).

Table 2. II scenario: RPR potential of Alytus region based on the results of a study in Flanders, Belgium [7]

2 scenario	Population in Alytus ragion in 2020	R		
	ropulation in Alytus region in 2020.	Qantitative goal		
	166 135	2022 m 7 k/person	1163 t	

#### Assessment of different scenarios using WRAP tool

The tool allows to assess the impact of textile, furniture, and WEEE item groups only; therefore, the impact of the other item group in Scenario 1 will be assessed by selecting the *all-items* option, assuming that the other item group consist of a variety of materials corresponding to the mix of furniture, textile and WEEE.

Prior to the start of PR activities in the sorting centers of the Alytus region, furniture was disassembled: wooden parts recycled (51 percent) and the rest disposed of by landfilling (49 percent). Textiles are most often disposed of by landfilling. In relation to the predominant material, other items are accounted for as secondary raw materials at sorting centers at the time of acceptance and later are sent for recycling as all WEEE, so the PR of other items and WEEE is compared to recycling.

The reference indicator for the environmental impact assessment of the PR is the environmental, economic and social impact of 1 t of selected items [16], which will be used to assess the environmental impact of the RPR of the three quantitative scenarios described above.

The environmental impact is assessed through GHG equivalent CO2 (tCO2eq) emissions, resource consumption (t) and fossil fuel energy consumption (eq MJ). The economic impact is assessed through the incurred (+) / avoided (-) costs of the selected waste management activity



(EUR), and the social impact is assessed through the number of created (+) / cut (-) jobs (full-time).



The impact indicators of 1 t reveal (Figure 2) the R and PR of all item groups, compared with recycling and disposing, have the highest positive value in terms of the environmental aspect. Speaking of the economic aspect, PR is a financial resource-intensive activity, while R is the least financial resource-intensive activity. Speaking of the social aspect, the number of jobs created for R and PR activities depends on which item groups are R and PR (e.g., PR of textile products creates fewer jobs if compared with recycling, and, in case of furniture PR, the number of jobs created is higher).

Moreover, based on the indicators of 1 t and the quantitative potential of each scenario, the environmental, economic and social impact of the PR on the environment of all three

scenarios has been assessed, providing an example for comparison, demonstrating the environmental impact in case the quantitative potential of the items in each scenario was managed using the previous management methods (i.e., the aforementioned ratio of recycling, incineration and landfilling in each group of items) in the absence of PR activities.



Fig 3. Comparison of 0 - 2 scenarios

The assessment results of Scenario 0 demonstrated the RPR activities, started in the Alytus region in 2020, had a positive environmental impact if compared with the previous methods for used item management: having prepared around 76 t of waste for R, the GHG emissions lowered fifteenfold, as well as the volume of resources used, and the amount of electricity consumed shrank by 8.6 times if compared with the recycling and disposal of the same amount of waste. In addition, around 0.2 percent (31 t) of waste did not end up in a landfill

(17,102 t of waste was disposed of by landfilling in 2020) [20]. However, due to greater environmental efficiency, the costs incurred grew by 2.8 times, and the number of jobs was not boosted because of the PR activities. Indeed, the number of new jobs has a tendency to grow if the quantity of PR waste grows because the number of jobs increases by 1.04 times due to PR activities.

In case of Scenario 1, the amount of waste disposed by landfilling drops by 7.8 percent (1,347 t) (17,102 t of waste was disposed in 2020), and the overall prepared R flow (around 3,370 t) constitutes about 5.2 percent of the waste managed in waste management facilities of the ARWMC (72,108 t of waste was managed in 2019) [20].

The positive environmental impact of Scenario 1, compared with the current management methods of this flow (recycling and disposing), would be the following: the GHG emissions dip by 2.2 times, the volume of resources used shrinks by 5.3 times and the amount of electricity consumed dips by 4.8 times. However, due to greater environmental efficiency, the costs incurred would inflate by 2.6 times, and the number of new jobs would climb up by 1.2 times.

In case of Scenario 2, the amount of waste disposed by landfilling would edge down by 2.7 percent (476 t) (17,102 t of waste was disposed in 2019) [20], and the whole PR flow (1,163 t) would comprise 1.6 percent of the waste managed in waste management facilities of the ARWMC (72,108 t).

The positive environmental impact of Scenario 2, compared with the current management methods of this flow, would be the following: the GHG emissions dip 7.5 times, the volume of resources used goes down 2.3 times and the amount of energy used drops 4.9 times. Higher environmental efficiency would lead to 2.7 times higher costs, but, at the same time, the number of new jobs would expand by 2.3 times.

The proportional environmental impacts of Scenario 0 and Scenarios 1-2 differ because the assessment of Scenario 0 is conducted in the light of the actual situation in 2020 and a small amount of waste, while other scenarios are assessed in terms of the impact on the projected quantity of items with different item group proportions that have different environmental impacts.

Taking into account the fact that the quantity of waste in the Alytus region is growing by 20 percent annually and the fact that it is planned to PR 90 t of items in 2021, the results of Scenario 2 can be achieved in the Alytus region in 18 years (2039) and Scenario 1 - in 22 years (2043).

In all scenarios, it is observed that the economic activity costs of PR are several times higher than of those waste management methods applied instead of PR. In addition to PR activities in the Alytus region, environmental educational activities are carried out; therefore, a certain combination with direct R promotion/popularization activities could significantly reduce these costs.

Assessing PR from a social point of view, the more waste is PR, the more jobs are created, compared with recycling and disposal. In case of Scenario 2, the number of new jobs created would be raised by 40 percent, and, in case of Scenario 1, this number would skyrocket by 70 percent.

In addition, assessing the number of additional jobs created for PR activities, it is important to take into account the environmental impact of PR of 1 t of waste from various groups, according to which only the PR activities of WEEE and other items create additional jobs, if compared with other waste management options. For this reason, from a social point of view, it is important to PR as many WEEE and other items as possible.

#### DISCUSSION

Significant indicators of the WRAP tool are the item R duration, what products (new or used) or services (e.g., laundry) are replaced or not changed at all (e.g., a free item received by a low-income individual does not replace an unnecessary or new item because she/her has no budget for it). In Lithuania, there is no data on how long items are used, especially second-hand products, and what products they replace; therefore, when analysing the possible PRP impact in the future or planning these activities, it is useful to assess these criteria (e.g., by conducting a survey of residents and other stakeholders).

### CONCLUSIONS

In CE, prolonging the life cycle of a product is one of the major ways to manage resources efficiently, and one form of its implementation can be the PR of products, and it can be developed along the lines of all three aspects of sustainability.

As most EU countries do not have experience in assessing the RPR potential, this methodology has been composed on the experience or specific examples of different countries to cover all three sustainability aspects. The methodology is the most useful when used as an initial tool for assessing the RPR potential when there is no experience in developing this activity in a given territorial unit (city, municipality, region or state).

In a specific case of application of the methodology, in order to quantitatively investigate the PRP potential in a municipal waste management system, it is useful to analyze used item suitability for PRP and look into the morphological composition of mixed municipal waste in the investigated territorial unit's sorting centers or other facilities (where the flow of RPR waste was assessed using the MFA or other method).

Following these studies, the assessment of the PRP potential in Scenario 1 could be based on the real proportions of eligibility for PRP in waste management processes suitable for this activity and compared with Scenario 2, which is based on indicators of a long-term, successful practice.

In the Alytus region, based on the current volumes of PR (76 t in 2020) and applying Scenario 2, PR of about 1,163 t of waste is possible by 2039 (i.e., the volume of waste disposal by landfilling drops by 2.7 percent (476 t), while about up to 1.6 percent of waste is taken back for R). In Scenario 1, the amount of waste ending up in landfills would go down by 7.8 percent (1,347 t) by 2043, and the total prepared R flow (about 3,370 t) would make up about 5.2 percent of all the waste managed at waste management facilities of the ARWMC (in 2020, 72,108 t was handled).

The higher financial costs incurred during PR activities can be reduced by promoting direct R, for example, through mutual exchange, online sales, donations to charities (e.g., PR of 1 t of furniture – EUR 405 and R – EUR 6.16); therefore, it is useful for waste management organizations to consider PR as one of the measures to promote waste prevention through the promotion of direct R.

Considering the social aspect, in Scenario 1 and Scenario 2, PR creates more jobs compared to the waste management activities performed instead of PR (recycling and disposal). However, this indicator may decrease or increase depending on the type of waste PR and the type and proportion of waste management methods (recycling, landfilling or incineration) used prior to the PR activities.

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# **VERMI-REMEDIATION OF HEAVY METALS: A REVIEW**

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#### ABSTRACT

Heavy metal pollution is one of the most important environment problems on a global scale. Heavy metals contamination of the soil contributes to soils degradation, reduction of agricultural production and pose a serious threat to safety of agricultural products and human health. Ecological-biological engineering is increasingly being used to solve environment pollution all around the world. The main aim of the present study is to review the remediation of heavy metals in soil through environmentally friendly method using earthworms. Literature review was used as a research methodology. Vermiremediation is very promising and eco-friendly removal method to address soil contamination with heavy metals, since earthworms tend to bioaccumulate heavy metals in their tissues, even at low soil concentrations. Earthworms due to direct contact with soil can effectively bioaccumulate heavy metals such as mercury, cadmium, lead, molybdenum, arsenic, barium, copper, iron, zinc etc. The rate of bioaccumulation of different metals depends on metal bioavailability, species of earthworms, time of exposure and environmental factors. Vermi-remediation has many advantages over traditional remediation methods, such as lower economic and energy costs, and improves soil quality. Based on a comprehensive literature review, vermi-remediation was identified as one of the best sustainable, natural and environmentally friendly technologies for the treatment of soil contaminated with heavy metals. However, vermi-remediation application in the context of redevelopment of contaminated sites is not well studied and has some limitations, so further research is needed.

Keywords: bioremediation, vermi-remediation, heavy metals, earthworms

## **INTRODUCTION**

Heavy metal pollution of the environment is one of the major environmental problems in the world [1, 2]. It is reported that more than 10 million contaminated sites exist worldwide, with more than 50 % of the sites contaminated with heavy metal(loid)s [3]. Heavy metals have both natural and anthropogenic sources in the environment. They naturally occur because of volcanic eruptions, forest fires, sea-salt sprays, rocks and soil decay. Major heavy metal sources are anthropogenic, like mining activity, industry, transport, application of agricultural fertilizers and pesticides, household and industrial waste, wastewater and sewage sludge [4, 5]. Heavy metals are not biodegradable and therefore accumulate in living organisms [6]. It is also very important that the mobility of heavy metals and their toxicity are greatly influenced by environment conditions. In addition, metals can migrate and contaminate soil and groundwater [7].

Heavy metal contamination of soils not only poses a critical risk to ecosystems, but also contributes to soil degradation, diminishing agricultural production and poses a serious threat to agricultural product safety. Thus, heavy metal contamination of soil poses a critical risk not only to the state of ecosystems but also cause adverse health effects to humans, including cardiovascular diseases, neurologic and neurobehavioral disorders, developmental disturbance, diabetes, hematologic and immunologic disorders and various types of cancer [8, 9, 10].

Ecological-biological engineering is increasingly being used to solve environment pollution problems in the world. There are emerging trends to embrace nature based solutions (NBS) as a way to render energy and resource efficient environmental pollution reduction, as well as enhancing remediation resistance to global environment change [11, 12]. In recent years scientists and engineers are trying to create cost effective technologies wich includes living organisms for cleaning of polluted sites. NBS for remediation, such as phytoremediation or vermi-remediation, offer many environmental, social and economic advantages in comparison with traditional methods [13].

## HEAVY METALS VERMI-REMEDIATION OF HEAVY METALS

#### **Heavy metals**

Heavy metals are divided into 2 classes: essential and non-essential. Essential heavy metals such as Co, Cr, Cu, Fe, Mn, Ni and Zn are considered to be very important trace elements, but at high concentrations they become dangerous and toxic. From a toxicological point of view, heavy metals such as Cd, Cu, Pb, Hg and Zn are considered to be among the most dangerous, but their effects to living organisms depend on the species, the chemical form of the metal, bioavailability, dose, duration, environmental conditions and abiotic factors [14,15].

Heavy metals exist in soil in various forms: dissolved ions (e.g.  $Cu^{2+}$ ,  $Cd^{2+}$ ,  $CrO_4^{2-}$ ,  $Cr_2O_7^{2-}$  and  $MoO_4^{2-}$ ) and organic complexes in soil solution (e.g.  $Cu^{2+}$ ,  $Pb^{2+}$  ir  $Hg^{2+}$  binds to the dissolved organic element), exchangeable ions (e.g.,  $Cu^{2+}$ ,  $Zn^{2+}$ ,  $Cd^{2+}$ ,  $Ni^{2+}$  ir  $Pb^{2+}$ ) adsorbed on soil solids and co-precipitated as part of soil solids (e.g.,  $Cd_3(PO_4)_2$ , ZnS, PbCO<sub>3</sub> ir HgSO<sub>4</sub>). These three heavy metals forms mutually maintain thermodynamic equilibrium activity and concentration, while insoluble sediment is the predominant form. However, it's not the total concentration of heavy metals that is important in the soil, but the reactive part, because it determines their bioavailability and toxic effects to biota. Distribution of forms is influenced by soil pH, reduction potential, presence of Fe/Mn oxides, organic matter and other cations and anions in the soil [16].

Soil pH is considered to be a major factor influencing heavy metals solubility, bioavailability in soil. Lower soil pH increases the concentration of heavy metals in soil solution, reducing their adsorption to organisms. As soil pH decreases, the amount of H<sup>+</sup> ions increases, which increases the capacity of cation exchange between heavy metals [17]. At the most common soil pH range, heavy metals can be divided into two categories: high mobility - Cd, Ni and low mobility Zn, Cu, Cr, Pb [18]. Research has shown that some metal cations (Cd, Cu, Hg, Pb, Cr, Fe, Mn and Zn) are more soluble and available in low pH soil solutions [19, 20]. It is important to note, that lowered soil pH doesn't increase activity of all heavy metals - the solubility of cations increases at lower pH values, when anions are more soluble in alkaline pH ranges due to sorption in solid soil phases [21, 17].

Soil contamination with heavy metals is a major scientific and technological challenge as heavy metals cannot be broken down into less or non-hazardous products. Heavy metals persist in environment for a really long time after they're introduced, depending on the type of metal and soil. Therefore, heavy metals clean-up requires their removal from the soil, their sequestration or immobilization. Heavy metals decontamination or removal from a certain location is a complex process. Remediation methods can be applied in two ways, in-situ and ex-situ. In-situ remediation does not require excavation and transport of the contaminated soil to off-site treatment facilities. Because of that, environment disturbance is minimized, exposure to the contaminants is reduced, and the treatment may cost significantly less than ex-situ remediations. Environment factors affects remediation, so field conditions have to be carefully considered. Ex-situ soil remediation involves excavation of soil from the contaminated site. Comparative to in-situ remediation, ex-situ treatment requires additional costs for soil excavation, transportation, disposal, and site refilling, but in this way better results can be achieved during shorter time [22, 16].

Current remediations of heavy metals contaminated soil processes are divided into 3 groups: physical, chemical and biological, which may be used in combination with one another [22, 23, 24]. Cleaning mechanisms are based on two basic principles. The first one is the complete elimination of pollutants, second is the conversion of pollutants into less harmful forms using engineering technology [25]. Main key factors, which determine the successful and practical application of remediation technology in the field conditions are cost, societal and environmental acceptability aspects. Management of soil pollution is a major economic challenge. Traditional physico-chemical methods of soil remediation can be applied to heavily contaminated soils, but only in small areas [26]. The application of these methods are limited due to high energy requirements and adverse effects on soil structure, productivity and biota. While biological treatment methods (bioremediation) are possible in low to medium pollution soils, which usually takes longer but they have numerous environment, social and economical advantages. Besides, bioremediation can be applied without any or very little human involvement [27, 24].

### Vermi-remediation

Vermi-remediation is the use of earthworms to clean up contaminants from the soil environment. Vermitechnology process is used as a preferable option to stabilize various kinds of solid wastes due to cost effectiveness, simplicity and nutrient availability, also it is an effective technology in reducing the toxicity of industrial wastes [28]. Earthworms importance has been highlighted not just in the fields of waste management, but also in environmental conservation, organic farming and sustainable agriculture. Earthworms among all soil dwelling invertebrates play a crucial role in soil function [29, 30]. Earthworms can improve soil properties and structure, increase microbial populations and bioactive metabolites. They significantly contribute to organic matter content, soil fertility, increase mineral N in soil, readily exchangeable phosphorus, potassium, calcium and magnesium, improves carbon fixation by plants and soil formation itself [31, 32, 28]. Earthworms also reduce the amount of pathogens in the soil because their coelomic fluid has antibacterial properties and they also uses some protozoa, bacteria and fungi as food source [33, 34, 35, 36].

Among biological remediation technologies focused on recovering degraded soils and cleaning contaminated sites, earthworms and their products (vermicompost) usage has emerged as a promising environment friendly approach. Vermi-remediation is really efficient method for cleaning sites contaminated with heavy metals, including low concentration polluted sites, because earthworms tend to bioaccumulate heavy metals in their tissues even at low soil concentrations [35, 34]. However, this can't be apply to all metals. For example, among heavy metals nickel does not normally accumulate in earthworm tissues even after prolonged exposure [37]. Many scientific studies proved that earthworms can readily bioaccumulate heavy metals (e.g., mercury, cadmium, lead, molybdenum, arsenic, barium, copper, manganese, calcium, iron, zinc) and other pollutants because of direct contact with soil, both externally via absorption through the skin and internally by adsorption to the digestive tract [38, 33, 39].

Heavy metal accumulation by earthworms is usually quantified as BAF, which is the ratio between the concentrations of metals in earthworms and metal concentration in the soil substrate. The heavy metal bioaccumulation factor (BAF) was determined in descending order: Cd > Mn > Ni > Zn > Pb > Cr > Fe. Bioaccumulation levels of different metals are variable due

to differences in metal bioavailability [33, 40]. Bioavailability is dependent on earthworms species, exposure time and environmental factors - soil pH, texture, moisture content, cation exchange capacity, temperature, root excretion (exudates) and nutrient content, which influence solubility (pH and reduction) and formation of a metal complex with soil organic matter. Application of vermi-remediation is most severely limited by the climate. There are very little information on how climate change affect the risk of heavy metal pollution to soil organisms [36, 29, 41, 19].

In order to increase the efficiency of vermi-remediation, it can be combined with other purification techniques, but then cleaning process gets more complicated [24]. For example, the addition of peat, compost, plant ash (biochar) during bioremediation improves the CEC of soil cation exchange, increases the number of sorption sites, reduces the mobility of metals, and promotes higher binding capacity. Soil CEC levels increase with soil molarity, while metal ion availability decreases. Thus, the higher the CEC, the higher the sorption and immobilization of metals, and the lower the CEC, the higher the availability of metals [42].

#### Earthworms characteristics and growth conditions

The earthworm species are generally classified into three ecological groups. These include epigeic earthworms that both feed and burrow in the litter layer on the soils surface, endogeic earthworms that primarily inhabit the top soil rich with organic matter [43], anecic that moves both vertically and horizontally in the soil and that form burrows in lower compartments of the soil profile [44]. Some earthworm species can survive even in heavily contaminated soil and are prone to accumulation because of differences related to ecological groups or physiological tolerance to heavy metals [44, 45].

Variety of earthworm species are investigated, with *Eisenia fetida* being by far the most practise utilised, because they are very effective for metalliferous contaminants bioaccumulation. Other earthworms species that are used for vermi-remediation are *Allobophora chlorotica*, *Aporrectodea tuberculata*, *Dendrobaena rubida*, *Dendrobaena tetraedra*, *Lumbricus rubella* and *Lumbricus terrestris* [46, 33]. There are many studies, where bioacumulation of metals by individual earthworm species were examined, but there are lack of experiments on accumulation of metals by different species in the same soil.

Environmental condition affect to earthworm population density, their distribution and activity. Most critical factors that regulate earthworm population are soil type and organic matter content, pH and moisture. Environmental conditions preferences vary depending on species, but they have adapted to survive in contaminated environments. Soil moisture is important factor, because earthworms respire through their moist skin. Earthworms are more active in moist soil than in dry. Excessive quantity of moisture might be lethal, because it creates anaerobic conditions (it takes a place of dissolved oxygen). Optimal moisture for growth and development of earthworms is 50-70 % water holding capacity (WHC). Temperature affects the respiration, growth, metabolism and reproduction of earthworms. Optimal temperature is 20-25°C, but they can tolerate a temperature range between 5-29°C [44, 47].

Earthworms are sensitive to soil pH. Neutral soil pH is preferred by most of species, but they can tolerate pH range from 4.5 to 9.0. After soil passes through the earthworm gut, soil pH adjustifies to ~ pH7 [47, 48, 6]. Organic matter content in soil has impact to vermi-remediation efficiency. Organic material is good energy source for earthworms. Several studies showed that if organic matter in the soil is low, higher number of earthworms can't be supported and the toxicity of heavy metals to earthworms increases, leading to mortality and reproduction disturbance rise [49, 50, 51]. However, there are some opposite evidence that organic matter addition to soil might reduce the efficiency of vermi-remediation [52]. Further analysis is strongly needed.

## CONCLUSION

Soil contamination with heavy metals has a significant negative impact on the environment and human health, as heavy metals are not biodegradable and have a really long lifespan. Soil bioremediation methods like vermi-remediation have many benefits over traditional ones, such as environment, energy, social and economical.

Vermi-remediation is suitable cleaning method of sites contaminated with heavy metals, because earthworms can survive in contaminated soils and accumulate heavy metals such as Cd, Cu, Zn, Pb and various other metals in their tissues even at low contamination sites. Vermi-remediation affects the distribution and concentration of heavy metals in soil fractions therefore leads to soil quality improvement.

Many species of earthworms are suitable for vermi-remediation process, while *Eisenia fetida* being by far the most widely used in practice. Environment factors, especially temperature and soil moisture, differently affect the heavy metals bioaccumulation in earthworms depending on specific elements and their species. There are a great need for research to assess the effects of climate change on vermi-remediation and other bioremediation technology sensitivity and efficiency. Recommendations on the future application and management of this method is much needed, because bioremediation strongly depends on environmental conditions.

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# AN OVERVIEW OF SIDERATE PLANTS PHYTOREMEDIATION POTENTIAL FOR PETROLEUM HYDROCARBONS CONTAMINATED SOIL USING VARIOUS BIOLOGICAL ADDITIVES

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#### ABSTRACT

Soil pollution is a widespread problem in the world. In Europe, according to the European Environment Agency, the total number of potentially contaminated sites is around 2.5 million, of which around 350,000 are considered to be highly contaminated. The most common soil pollutants are petroleum hydrocarbons. According to the Lithuanian Geological Survey, more than 12,000 potential pollution spots have been identified in the country, more than 5000 are related with petroleum hydrocarbons pollution.

Various physical, chemical and electrokinetic methods are used to reduce soil pollution, but biological methods, in particular phytoremediation, have recently received considerable attention. This method is relatively inexpensive and environmentally friendly, in most cases does not generate new waste and secondary pollution compared to other conventional treatment methods.

Assessing all the requirements for phytoremediation, a very promising group of plants are siderate plants, most of which have symbiotic nitrogen – fixing bacteria. Siderates, especially legumes, have an advantage over non – nitrogen fixing plants because of their inherent ability to fix nitrogen, legumes do not have to compete with microorganisms and other plants due to limited soil nitrogen reserves in contaminated areas. Moreover, during the siderates growing soil is decontaminated and at the same time the soil fertility can be restored or improved. The effectiveness of siderates based phytoremediation depends on the species of used plants, the composition of contaminants to be treated, their concentration and environmental factors. Various technological solutions or additives may be used to increase the efficiency of bioremediation, such as growth promoters, nutrients, inoculum of microorganisms.

A pilot scale phytoremediation test of fuel oil contaminated soil using *Medicago sativa* (alfalfa) and oiloxidizing microorganisms as an additive shows that the use of such an additive increases the rate of decomposition of the contaminants.

The aim of this paper is to review the potential of different siderate plants species in petroleum hydrocarbons contaminated soil bioremediation, based on their morphological and phytoremediation properties and identify the effects of different biological additives in promoting the phytoremediation process.

Keywords: soil bioremediation, petroleum hydrocarbons, siderates, legumes, biological additives

### **INTRODUCTION**

Petroleum hydrocarbons are used for various purposes, such as a lubricant for machines and fuel for cars and heaters, and it is an essential material for daily life. Petroleum hydrocarbons are among the most common soil and water pollutants in the world. Due to the wide variety of compounds and their different ecotoxicity and persistence for degradation, petroleum hydrocarbons can be identified as priority soil contaminants along with heavy metals. Various physical, chemical and biological methods are used to remove petroleum hydrocarbons from the soil. The method of decomposing pollutants using microorganisms and plants in a soil or other medium is called bioremediation. Petroleum hydrocarbons are broken down in the natural environment by various types of microorganisms, and plant roots promote the biodegradation of these pollutants [1]. They can use petroleum contaminants as a food source and naturally decompose them into environmentally harmless compounds.

Sometimes, due to certain factors, such as high pollutant concentration, fractional composition or lack of nutrients, microorganisms are unable to efficiently decompose petroleum hydrocarbons, in which case the use of plants (phytoremediation) can greatly accelerate the soil remediation process, because the living conditions of microorganisms in the plant root zone and at the same time the ability to decompose contaminants are greatly improved. Various petroleum-resistant plants can be used for this purpose, such as *Medicago sativa*, *Onobrychis vicifolia*, *Galega orientalis*, *Trifolium pratense*, *Cajanus cajan* and others [2], [25].

Hydrocarbons phytoremediation success and effectiveness depends mainly on the soil type, plant species, conditions, microbial activities and the interactions between these factors. Although various species of plants and organisms for phytoremediation processes have been extensively studied over the past few decades, important attention needs to be paid to assessing and characterizing soil properties, which are important foundations for sustainable remediation and land use management.

Comparing to the destructive and expensive traditional methods (incineration, in - situ flushing, solidification and stabilization, etc.), phytoremediation is a relatively low cost alternative, recently used for the remediation of a variety of environments (soil and water), contaminated with heavy metals and/or petroleum hydrocarbons [3], [27].

This paper reviews the potential uses of siderate leguminous plants for the treatment of petroleum hydrocarbons contaminated soils and analyses various biological additives that can increase the phytoremediation efficiency. The results of a pilot scale test on the use of *Medicago sativa* and oil-oxidizing microorganisms inocula as an additive for fuel oil contaminated soil phytoremediation are also presented.

## **RESULTS AND DISCUSSION**

#### Leguminous siderate plants for petroleum hydrocarbons phytoremediation

The use of siderate plants for the phytoremediation process can significantly accelerate the efficiency of soil remediation due to the fact that these plants are less demanding of soil quality. Contaminated areas are often characterized by poor soil fertility, and legumes in the root zone have symbiotic nitrogen – fixing bacteria that allow the plant to grow [4]. At the same time the physical and chemical properties of the soil are restored and microorganisms that decompose petroleum hydrocarbons are stimulated. Many studies have shown that legumes are able to grow in petroleum contaminated soil and reduce the concentration of contaminants [5], [6], [26].

The success of phytoremediation is largely determined by the microorganisms stimulated by exudates, secreted by plant roots, and many studies have confirmed this. The effectiveness of soil remediation is influenced by many factors, soil structure and type, plant species, different microorganisms and their communities. Due to the different resistance to contaminants, morphological and physiological properties and the ability to coexist with associations of different microorganisms, a number of studies are still needed to select the plants with the greatest potential for cleaning petroleum hydrocarbons contaminated soils [7], [28].

The *Fabacea* plant family is worth mentioning when it comes to contaminated soil remediation. These plants are legumes that have organs in their roots called nodules that contain nitrogen-fixing bacteria. Due to this property, legumes are able to grow in different climatic conditions, tolerate infertile and degraded soils, those most commonly found in contaminated areas. Legumes are growing worldwide, there are over 18,000 different species [8].

Legumes of the Fabacea family have an advantage over other species used in phytoremediation when the soil is low in nitrogen. Due to the ability to fix nitrogen directly from the atmosphere, legumes do not have to compete with other plants due to limited nutrient reserves. The most important point is that nitrogen-fixing bacteria living in the root zone must be resistant to soil contaminants. Numerous studies have been performed and there are confirmations that nitrogen-fixing bacteria (rhizobes) can survive in soils that are contaminated with different petroleum hydrocarbons and successfully fix nitrogen [9], [29].

Legumes can be used for phytoremediation directly due to the decomposition of petroleum hydrocarbons, or the properties of these plants can be used to improve soil structure and yield when grown in combination with other plants that have been shown the potential of soil decontamination, but are intolerant to nutrient deficiencies. Legumes are also often used in uncontaminated soils as an excellent green manure, capable of rapidly increasing the amount of nutrients in degraded soil. Such a strategy can significantly improve the soil cleaning process, as microorganisms will also be stimulated. Costs for fertilizing depleted soil with fertilizers will also be reduced [10].

# The experience in the use of legumes for petroleum hydrocarbons contaminated soil phytoremediation

A number of studies have been performed using legumes for phytoremediation of petroleum contaminated soil. Efficacy results for the use of these legume plants are presented too. The most common leguminous plant species in the literature review are: *Medicago sativa*, *Cajanus cajan*, *Lablab purpureus*, *Onobrychis viciifolia*, *Galega orientalis*, *Trifolium repens*, *Onobrychis antasiatica* and other [4], [7], [30].

One of the most important morphometric parameters for phytoremediation process is plants seed germination rate in contaminated soil. A comprehensive cluster analysis of seed germination in kerosene of different plant families and species was performed (kerosene is a complex mixture of aliphatic and aromatic hydrocarbons ( $C_6 - C_{16}$ )). In this case, 31 cultivated plants from 11 families were studied. Some relationships between seed germination and plant taxonomy have been revealed. Plants of the *Fabaceae* family (legumes) were included in the three most pollutant resistant groups by cluster analysis. The response of plants of the *Fabaceae* family to kerosene was species specific. The first parameter  $C_{75\%}$  indicated the concentration of kerosene in the soil at which the plants germinated 75 %. The second parameter ( $V_{7\%}$ ) shows the relative germination of seeds when the concentration of kerosene in the soil was 7%. [11]. The main parameter of a plant that determines its potential in the phytoremediation process is the decomposition capacity of the pollutant.

According to many studies, legumes of the *Fabaceae* family have been shown to promote the degradation of various petroleum hydrocarbons, including fuel oil, diesel, crude oil, PAHs, and others [12], [13]. Studies show that plants in the *Fabacea* family have achieved a greater potential to degrade PAH compared to other plant families. The following plant species (*Medicago sativa, Melilotus officinalis* and *Trifolium pratense*) were tested [9]. The leguminous *Onobrychis viciifolia* species stands out as a plant with tolerance in soils contaminated with total petroleum hydrocarbons pollution level of 2,86 % and have a phytoremediation potential [14]. In some studies, the pollutant degradation rate in soil has been shown to be lower under legumes, however, the final contaminant concentration at the end of the experiment was similar to or lower than in cases where non-leguminous plants were used. [15].

In soils with a crude oil contamination of 3 %, the resistance of legumes (*Glycine max*, *Lablab purpureus*, *Medicago sativa*, *Arachis hypogea*, *Cajanus cajan* and *Pheseolus vulgaris*) was tested. The degree of resistance depends on the type of plant. The potential of different plant species to decompose different chain length petroleum hydrocarbons was also mentioned. The short chain oil components (C<sub>1</sub>-C<sub>10</sub>) were completely degraded in the root zone of *P*. *vulgaris*, almost completely degraded by *A. hypogea* 97,23 % and M. sativa 93,54 %. The higher decomposition efficiency of the oil fraction (C<sub>10</sub>-C<sub>20</sub>) components was observed in the soil where *G. max* was grown, the decomposition efficiency was 92,89 %. In contrast to the decomposition of C<sub>1</sub>-C<sub>10</sub>, *P. vulgaris* decomposed a small number of C<sub>10</sub>-C<sub>20</sub> oil components, the efficiency was only 13,42 %. Less degradation of this fraction was also observed and in the case of *M. sativa* 40,18 % and *A. hypogenesis* 28,35 %. The components of the C<sub>21</sub>-C<sub>30</sub> fraction were found to be best degraded by *G. max*, as much as 93,66 % [7].

#### Biological additives for the promotion of the phytoremediation process

Most often, contaminated soils have low levels of nutrients, and this factor can be a limiting in the survival of plants and microorganisms, and even more limiting in the efficiency of decontamination [16].

Based on the material published by various authors, the phytoremediation process of petroleum hydrocarbons contaminated soil can be stimulated by the use of various additives. Various substances can stimulate plants or native microorganisms. Additives can also introduce new microorganisms into the soil, and some additives can alter the properties and bioavailability of the contaminant, thus speeding up the decontamination process [17]. Several groups of additives for the promotion of petroleum hydrocarbons decontamination in soil can be found in the literature:

- Low molecular weight organic acids. These compounds are detected in exudates secreted by plant roots. It is known that some of these organic compounds are capable of enhance the desorption of petroleum hydrocarbons from soil, thus altering bioavailability. Citric acid, malic acid, and oxalic acid are found in plant root exudates, when plants are growing in heavily contaminated soil, and these compounds have great possibility to improve the biodegradation of the contaminant, and their additional incorporation can speed up the process efficiency [18].
- **Biosurfactants** (Surfactants of biological origin) are a group of amphiphilic compounds consisting simultaneously of both hydrophilic and hydrophobic parts of their molecular structure. This structure of biosurfactants can improve the solubility of hydrophobic contaminants, thus facilitating their bioavailability to rhizosphere microorganisms. The

use of synthetic surfactants is not recommended due to their toxicity to microorganisms [19].

- **Biochar** (charcoal) is the solid product of pyrolysis (the thermal degradation of biomass in the absence of oxygen) usually used as a soil amendment in agriculture. The use of biochar can not only improve plant growth, retain nutrients, but also stimulate the growth of oil – oxidizing microbes, which in turn can stimulate rhizodegradation efficiency [20]. Another biochar effect, this additive can strongly absorb free petroleum hydrocarbons and their metabolites, which will be gradually degraded by microorganisms [21].
- **Inoculum of petroleum hydrocarbons oxidizing microorganisms**. Local microbial activity can be stimulated, but it is widely recognized that microbial species have limited enzymatic activity and can therefore degrade a small range of compounds, so the incorporation of a consortium of microorganisms into contaminated soil has a greater potential to degrade hydrocarbon mixtures. Studies show that the introduction of consortia of microorganisms has a better effect than the use of single strains [22].
- **Biodegradable waste and waste products**. Biodegradable waste such as animal manure, sewage sludge as well as compost, biohumus, etc. provide multiple benefits in phytoremediation of petroleum hydrocarbons. These substances enrich the contaminated soil with nutrients, organic carbon and active microorganisms, promote the growth speed of plants and microbes and increase the metabolic capacity [23].
- **Bulking agents** (chopped straw, hay, bark, wood chips etc.) these amendments can improve the rhizoremediation rate of petroleum hydrocarbons by stimulating the microbial activity via increasing the soil porosity and oxygen uptake [24]. Also it is beneficial due to the gradual release of nutrients in the soil.

# The results of a pilot test for phytoremediation of fuel oil contaminated soil using *Medicago sativa* (Alfalfa) and oil – oxidizing microorganisms as an additive

A pilot phytoremediation test of fuel oil contaminated soil was recently performed. The aim of the test was to determine the potential of leguminous plant *Medicago sativa* (Alfalfa) to remediate fuel oil contaminated soil. It has also been evaluated whether the use of oil – oxidizing microorganisms as an additive will accelerate the rate of decomposition of pollutants. The commercial microbiological preparation BFL 6000HC was used.

Alfalfa was tested at an initial contamination of 4 and 6 g/kg. Soil samples were taken 30, 60, and 90 days after the start of the experiment. Gas chromatography method was used for the determination of petroleum hydrocarbons concentration in the soil. During the experiment, each test group had three replicates and the data in the graph are the average of three replicates. The results show that after 90 days test, group with an initial contamination of 4 g/kg without microbial inoculum, had the 60.75 % degradation efficiency of fuel oil degradation, with microbial inoculum the efficiency was 77.18 %. In the test group with 6 g/kg initial soil contamination even better results were obtained, without microorganisms the efficiency was 79 %, with the inoculum the efficiency was 85 %. The test results are shown in Fig. 1.



Fig.1. The effect of *Medicago sativa* (alfalfa) and oil – oxidizing microorganism inoculation for fuel oil decomposition in soil. (number 1 inicial fuel oil concentration, number 4 residual fuel oil concentration after the treatment).

## CONCLUSIONS

This paper presents a review of the literature on the use of legume plants for the petroleum products contaminated soil phytoremediation. According to various studies, the use of legumes is promising due to their resistance to pollutants and their ability to fix atmospheric nitrogen in the root zone. However, due to various morphometric properties, such as seed germination and the ability to decompose specific petroleum hydrocarbons from the mixture, the phytoremediation potential of different legume species is also different.

There is evidence that the use of various biological additives, e.g. low molecular weight organic acids, biosurfactants, biochar, oil – oxydazing microorganisms and etc. rhizodegradation processes can be significantly accelerated. Positive effects can be obtained by stimulating plants, stimulating or adding new strains of microorganisms, as well as affecting the bioavailability of contaminants.

A pilot test was performed for phytoremediation of fuel oil contaminated soil using *Medicago sativa* (Alfalfa) and oil – oxidizing microorganisms inoculum as an additive. The obtained results show that *Medicago sativa* has the potential for phytoremediation to decompose petroleum hydrocarbons in the soil, the intensity of decomposition of pollutants increases when the inoculum of microorganisms decomposing oil products is added to the soil as an additive. The obtained results correlate with the data of other scientific researches, the use of petroleum hydrocarbon-degrading microorganisms as an additive to phytoremediation, promotes the rate of degradation of pollutants.

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# NITROUS OXIDE CONDITION IN THE COUNTRY'S RICE BASKET OF INDONESIA AFTER GREEN REVOLUTION

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#### ABSTRACT

The logic of the Green Revolution - spurred by the introduction of modern high-yielding rice crops was that food security was the most important factor in social development. That logic paid off with food supplies that have outpaced the dramatic population growth and urbanization over Indonesia, which has Java continued to be the country's rice basket, producing about two-thirds of the country's rice on roughly half the nation's rice fields, and an important source of nitrous oxide ( $N_2O$ ) emissions. In this study, we estimated N<sub>2</sub>O emissions using a DNDC (Denitrification-Decomposition) model derived by satellite database encompasses climate data (APHRODITE's), soil properties (WoSIS), and farm management practices in paddy fields start from 2005 to 2010. The results showed that the production of rice fields was 3.96 million t ha<sup>-1</sup> in 2005-2010. The annual precipitation and mean temperature were 2724.3 mm and 26.8°C, respectively, during the rice growing seasons. In line with that, the soil properties assessments such as soil moisture had a moderate influence on N<sub>2</sub>O emission on these sites. Process-based biogeochemical modelling, as with DNDC associated with satellite data, can help in identifying strategies for optimizing resource use, increasing productivity, closing yield gaps and reducing adverse environmental impacts. The statistical analysis showed that the precipitation ( $R^2$ = 0.35) and soil moisture ( $R^2 = 0.94$ ) was significantly affected on N<sub>2</sub>O emission, is 18.79 kg N ha<sup>-1</sup> yr<sup>-</sup> <sup>1</sup> during 2005-2010.

Keywords: Nitrous oxide, Paddy fields, Global change, Green revolution, DNDC model

## **INTRODUCTION**

In recent years, extreme events induced by global climate change such as tsunamis, hurricanes, heavy rain and drought, have been threatening hundreds of millions of people's lives. The international community is working hard to strengthen the control of global climate change. Therefore, as the main greenhouse gases, carbon dioxide ( $CO_2$ ), methane ( $CH_4$ ) and nitrous oxide ( $N_2O$ ), have been attracting scientists and government great attentions. Agricultural soils are the main source of the three gases. One phenomenon in the agricultural sector over the world, which has increased the productivity, mechanization tools, and chemical fertilizer practices, is Green Revolution. The logic of the Green Revolution—spurred by the introduction of modern high-yielding crops in the 1960s—was that food security was the most important factor in social development. That logic paid off with food supplies that have outpaced the dramatic population growth and urbanization across Asia for the last 30 years.

By the 1960s, with Indonesia now a republic, Java continued to be the country's rice basket, producing about two-thirds of the country's rice on roughly half the nation's rice fields. However, the Green Revolution would be something dramatically different, even in relatively bountiful Java. With the full-scale implementation of the Green Revolution through the BIMAS, or "mass guidance," program, the Suharto regime invested heavily in every facet of rice production. Along with the technical achievements that put more rice in the fields and food stores of farmers, the Green Revolution also brought a social and environmental revolution as

higher yields sustained a rapidly increasing population. In contrast, the unprecedented intensification that came with the Green Revolution brought fertilizers and pesticides, with them, the potential to dramatically reshape the environment such as GHG emission from agricultural sector.

According to IPCC [1], reported that CH<sub>4</sub> contributed 3.3 G t CO<sub>2</sub>-eq/yr and N<sub>2</sub>O 2.8 G t CO<sub>2</sub>-eq/yr. Of global anthropogenic emissions in 2005, agriculture accounted for about 60% of N<sub>2</sub>O and about 50% of CH<sub>4</sub>. It makes, quantification of greenhouse gas (GHG; CO<sub>2</sub>, CH<sub>4</sub>, and N<sub>2</sub>O) emissions from agricultural soils is essential for developing mitigation options and policies, such as in Indonesia, which has the fifth most populated country in the world and is a major producer of agricultural products [2], and the world largest island country, with the total area is 1,904,569 square kilometres (735,358 square miles) [3]. Those condition makes the direct measurement of greenhouse gas emissions through field observation as a normal method and used for inventory purposes is impractical as it would require many measurements to be made over large areas and for long periods of time [4].

One of the process models used to estimate N<sub>2</sub>O emissions is the DeNitrification-DeComposition (DNDC) model. The DNDC model is a biogeochemical model used to estimate soil GHG emissions and crop production. Although it was initially developed for conditions in the USA [5], it has been used for simulating N<sub>2</sub>O emissions worldwide, which has the core of DNDC was built up by integrating a group of biochemical and geochemical reactions commonly occurring in agroecosystems, which governed carbon (C) and nitrogen (N) transport and transformation in the plant-soil-climate systems, including CO<sub>2</sub>, N<sub>2</sub>O and CH<sub>4</sub> emissions, soil organic carbon (SOC) dynamics, and so on. DNDC is recognized as one of the most successful biogeochemical model, which is suitable for a wide range of agroecosystems across any climatic zone [6-8]. Subsequently, six long-term field data across the world were collected by Li et al. [9] and conducted to test the model's performance of simulating SOC dynamics. The simulation results were all consistent with the measurements. In addition, the DNDC with a few modifications can predict CH<sub>4</sub> emissions better from rice paddy soils in Japan [10]. Also, Babu et al. [11] used N<sub>2</sub>O and CH<sub>4</sub> emission fluxes observed from 10 different rice paddy experimental sites in Indian, with a less than 10% differences results between simulation and observation in the DNDC model.

If a biogeochemistry model was only to be of use at site scale, it might only play a limited role because almost all the serious eco-environment issues happened in a large scale and were managed or governed in regional scale. And thus, only the scientific results that obtained from the large scale or national scale can effectively promote establishing new policy or legislation. For national scales, DNDC has been used to estimate N<sub>2</sub>O emission up to 1.2 Tg N yr<sup>-1</sup> from croplands in America (Li et al., 1996) and predicted the net GHG emissions and the increase of crop yield next 20 years in rice production areas of China [12]. To the best our knowledge, the DNDC model to estimate N<sub>2</sub>O emission has not previously been studied especially after the BIMAS (adopted from green revolution) successfully implemented over 60 years in Indonesia. Therefore, the objectives of this study were to estimate the impacts of monoculture systems on rice productivity and N<sub>2</sub>O emissions under long-term climate, soil moisture, temperature, and supported by geographic information system (GIS) satellite databases, regulation, and policy of agriculture in Indonesia.

## MATERIAL AND METHODS

#### **Experimental site description**

The study site was at Cilacap regency, Central Java, Indonesia (7.45°S, 109.01°E) showed in Fig 1. the experiment was conducted during the rice growing periods in a whole year from January to December in five years starts from 2005 to 2010. The site is 6 m above the mean sea

level with a tropical monsoon climate with mean temperature 26.8°C and annual precipitation 2724.3 mm, which has collected from APHRODITE's (http://aphrodite.st.hirosaki-u.ac.jp/). About 80% of the precipitation occurs during the period from November to March as rainy season, while the dry season occurs from April to October. The soil of this experimental site can be classified as sandy clay loam, with bulk density 1.56 g cm-3, and pH 6.05, which has collected from WoSIS database (https://www.isric.org/). Paddy was sown by hand in with three times planting times in a year. The soil was ploughing with disk or chisel at 10 cm soil depth. For the treatment with fertilization, 300 kg urea-N per ha and 75 kg Phospate- per ha was applied on each planting times. The fertilizer application rates and timing were determined based on the No.40/Permentan/OT.140/4/2007 about recommendation for paddy fertilization in Indonesia [13].



Fig. 1. Study site location

# An overview: DNDC model

The Denitrification-Decomposition (DNDC) model is a widely studied process-based model for simulating C and N dynamics in agroecosystems [14]. The model framework incorporates four primary sub-modules including crop vegetation, soil/climate, decomposition, and denitrification/nitrification. It has been applied extensively to estimate greenhouse gas emissions, soil temperature and water dynamics, soil C and N cycling and crop growth under different ecosystems (i.e., cropland, grassland and forest system) [15]. In agricultural systems, it has been applied to simulate the effects of various field management practices including tillage, crop rotation and fertilization [16-18] as well as current & future climate scenarios [19].

## **Parameter input**

During the past three decades, the DNDC model has been independently tested and applied for soil C and N studies and suitable for a wide range of agroecosystems across climatic zones and 20 countries with promising results, but not implemented yet in Indonesia, specifically for  $N_2O$  emission. The input data supporting for the model runs include daily climatic data, soil property, land use, and management practices, as detailed in Table 1.
Parameter Unit		Parameter	Unit	
Location Site		Soil parameter		
Latitude		Soil Land use type		
Climate/weather parameter		Soil texture		
Daily air temperature	oC	Bulk density		
Daily precipitation (cm)	(mm)	рН		
Daily average wind speed	(m/s)	SOC content		
Humidity	(%)	Clay fraction		
Daily solar radiation	(MJ/m2/day)	Soil structure	kg C/kg soil	
N conc. in precipitation	(mg N/l or ppm)	NO3- concentration at surface soil	(m)	
Farming parameter		NH4+ concentration at surface soil	(0–1)	
Сгор Туре	(62 default types)	Field capacity	(mg/kg)	
Crop rotation	(no. crops per year)	Wilting point	(mg/kg)	
Planting and harvest date		Porosity	(WFPS; 0– 1)	
Cover and perrenial crop	(yes/no)	Hydro-conductivity	(WFPS; 0– 1)	
Annual N demand	(kg N/ha/year)	Microbial activity index	(0–1)	
Maximum biomass (kg/C/ha/year) prod.		Tillage, fertilizer, flooding, and manure		
Water demand	(g water/g dry matter)	Method, no. of applications, dates (0–1)		
N fixation index	(crop N/N from soil)	N in flood water		

Tabel 1. Input parameters of DNDC model [20]

# **Statistical analysis**

Statistical analysis conducted using one-way ANOVA analysis in the SPSS 20.0 package followed by the Duncan's test at the 0.05 level (p < 0.05) to determine whether there were any statistically significant differences between the diversified rotation treatments.

# **RESULTS AND DISCUSSIONS**

# **Production of rice**

Rice is the most important staple food crop for over 3 billion people in the world [21]. Global rice consumption is projected to increase from 450 million tons in 2011 to about 490 million tons in 2020 and to around 650 million tons by 2050 [22]. The total rice production in Cilacap was 3 million ton ha<sup>-1</sup>, for sufficient the rice consumption in Indonesia, where, supported by the intensive farming practice with high fertilization is widely adopted to increase crop productivity, and therefore, the dependence on fertilizers has continually increased in the rice cropping industry [23]. However, the increase of N fertilizer application can stimulate greenhouse gas (GHG) with global CH<sub>4</sub> emissions from paddy soils range from 31 to 112 Tg

 $y^{-1}$ , accounting for up to 19% of total emissions, while 11% of global agricultural N<sub>2</sub>O emissions come from rice fields [24-25].

### Precipitation, temperature, and soil moisture in the Study Sites

Nitrous Oxide (N<sub>2</sub>O) is one of the most important global greenhouse gases [26]. In contrast to other greenhouse gases, N<sub>2</sub>O is often released instantaneously and circumstantially from the soils, particularly after precipitation during drought season [27]. Fig. 2 presents the observed climate data. The daily mean air and soil temperature are 26.89 and 29.02°C, respectively; the highest daily maximum air and soil temperature was 28.15 and 29.96°C, while the lowest was 25.8 and 27.9°C. Precipitation was recorded which is the daily maximum precipitation was 27.99 mm on 3<sup>rd</sup> December, while the lowest on 11<sup>th</sup> August, is 1.26 mm day<sup>-1</sup>. Based on analysis start from 2005 to 2010 showed that the peak of rainy season between December – January, while the dry season around July – August. Temperature, along with moisture, is one of the most influential environmental factors affecting rates of nutrient cycling and production of greenhouse gases in soil [28].



Fig. 2. Seasonal changes of rainfall, **a**r () and s**a**l () temperature, and soil moisture during 2005-2010

# Nitrogen balance and Nitrous oxide emission

Soil N supplying capacity significantly decreased over time after N fertilization input 900 kg N  $ha^{-1}$  yr<sup>-1</sup> and the total input N is 1182.34 kg N  $ha^{-1}$  from rainfall N deposit, crop stub N, and N fixation. The N uptake by crops was 320.25, 43.51, 107.6, and 531 kg N  $ha^{-1}$ , for N leaching, N runoff, and NH3 volatilization, respectively. The average emission of N<sub>2</sub>O, NO, and N flux, are 18.8, 0.9, 105.3 kg N  $ha^{-1}$ , where, the fluctuative and seasonal changes of N<sub>2</sub>O emission during 2005-2010 has been showed in Fig 3.



Fig. 3. Nitrogen balance condition from N input and output



Fig. 4. Seasonal patterns of N<sub>2</sub>O emission

The relationship between nitrogen input and N<sub>2</sub>O emission established by Bouwman [29] motivated the concept of emission factor (EF). The emission factor is defined as a fraction of the nitrogen input released in the form of N<sub>2</sub>O within the current seasonal or annual period, where, the default emission factor of N<sub>2</sub>O for synthetic nitrogen averages 1.25%, ranging from 0.25% to 2.25% and N<sub>2</sub>O background emission is assumed to be 1 kg N<sub>2</sub>O N ha<sup>-1</sup> yr<sup>-1</sup> in the IPCC methodology [30].

Fig 4. Shows that the large emission peaks (0.98 kg N ha<sup>-1</sup> yr<sup>-1</sup>) occurred in the N treatments within one week after fertilization following rainfall was increased in 3<sup>rd</sup> planting times. There was also a lowest of N<sub>2</sub>O resulting due to dry seasons from May to August, where, below 0.05 kg N ha<sup>-1</sup>yr<sup>-1</sup>. These large N<sub>2</sub>O emissions occurred under dry and wet conditions when the soil WFPS ranged from 30% to 100%, which statistically analysis showed there is a high correlation between precipitation and soil moisture to N<sub>2</sub>O emission in paddy fields, is  $R^2 = 0.351$  and  $R^2 = 0.946$ , as showed in Fig 5 below.



Fig. 5. Correlation between precipitation and soil moisture affected on N<sub>2</sub>O emission.

According to Birch et al. [31] found that the soil drying and wetting cycles caused by precipitation stimulated the mineralization of soil organic matter, resulting in rapid soil carbon losses; such phenomenon was called the "Birch effect". The variations in precipitation distribution affect the biological activity of microbes and plants, thereby affecting the soil N dynamics and the corresponding soil N2O effluxes [32].

### CONCLUSIONS

We analysed N<sub>2</sub>O emissions from paddy fields that were consecutively measured for five years. The factors include nitrogen input, soil moisture, and precipitation were significantly responsible for seasonal changes of N<sub>2</sub>O. The total annual fertilizer-induced N<sub>2</sub>O emission was estimated to be 18.79 kg N ha<sup>-1</sup> yr<sup>-1</sup>. The highest N<sub>2</sub>O fluxes occurred after dry seasons and 3<sup>rd</sup> planting times.

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# SELECTION OF REGIONAL CLIMATE MODELS FOR USE IN HYDROLOGICAL MODELING OF LITHUANIAN RIVERS

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### ABSTRACT

Starting from the second half of the 19th century, due to increased industrialization, people began actively influence the climate of the planet, and as a result, we have been witnessing significant climatic changes in recent decades. At the same time, the formation of river runoff largely depends on the basin's climatic conditions; therefore, any climate change will directly affect it and can lead to catastrophic consequences. In order to be able to withstand or adapt to these changes, scientists have developed a number of global and regional climate models to predict future changes in accordance with various scenarios of human development. The predict climate data is used to assess the impact of climate change on rivers and their hydrological regime.

The aim of this study was to select a regional climate model that could accurately describe Lithuanian conditions by comparing simulated historical climate data with real observed data. Four regional climate models (RCMs) were selected for comparison: CCLM4-8-17 (in two driving model versions), SMHI-RCA4, WRF381P, RCA4 (in two driving model versions) - a total of six models. The daily model data was taken from the CORDEX database with resolution of 0.11 degree. Observed data were taken from two meteorological stations: Telšiai and Vilnius for the period from 1986 to 2005. For comparison, daily, monthly and annual temperature and precipitation indicators were taken as they are one of the main inputs for many hydrological prognostic models, such as the HBV (Hydrologiska Byråns Vattenbalansavdelning) model developed by the Swedish Meteorological and Hydrological Institute.

Initially, RCMs were compared with observed data by the difference in medians and ranges of selected meteorological variables of annual data sets. Statistical comparison of simulated and observed data was performed by statistical analysis methods (Pearson's correlation or Spearman's correlation and significance tests). The Wilcoxon test in the case of non-normal data distribution and the Pared t-test in the case of normal distributed data were used to determine whether the simulated data of each specific RCMs differed from the observation data in a statistically significant manner.

Significance test showed that data simulated by the RCA4 model based on NCC-NorESM1-M global model has the lowest difference with observation data compare to the other RCMs and suited to describe the region's climatic situation. However, it did not show the highest correlation compared to other models so it is not recommended to use for trends analysis. The best model for displaying daily and monthly trends based on correlation analysis data was the CCLM4-8-17 climate model in two versions, based on CNRM-CERFACS-CNRM-CM5 and MPI-M-MPI-ESM-LR global models. Downscalling methods could be used for all selected models for better adaptation of RCMs in the investigated region.

Keywords: Climate change, Regional Climate Models, CORDEX

# IMPACT OF OUTDOOR BLACK CARBON LEVEL TO INDOOR AIR QUALITY

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#### ABSTRACT

In the last decade, black carbon (BC) has gained particular attention around the world for its impact on regional and global climate change, air quality, public health and ecosystems. It is the most strongly light absorbing component of particulate matter (PM) with short atmospheric lifetime (days to weeks), and have the potential to affect human health. Due to its small size (less than  $2.5 \,\mu\text{m}$ ), it is easily inhaled and can enter the lungs, bloodstream and cause cardiovascular, respiratory and another diseases. Nowadays people in developed countries spend most of their time (~90%) in indoor environments (home, offices etc.) where energy-efficient buildings can create risks for indoor environmental quality and as a result for health of occupants. It should be noted, that to achieve low carbon emission buildings by 2050, at European and national levels, stringent targets for the necessary energy transition have been set. Study of outdoor impact to indoor air quality of pollutants plays an important role. Outdoor/indoor relationships of traffic and biomass burning-derived black carbon was determined in an urban background environment. Continuous real-time measurements of optical absorption by aerosol particles and equivalent black carbon (eBC) mass concentration were carried out at Vilnius for the cold period (from October to December 2020) using a Magee Scientific Company AethalometerTM, (model AE31 Spectrum, manufactured by Aerosol d.o.o., Slovenia. The results show that outdoor impact to indoor air quality is highly responsible. The durinal indoor eBC mass concentration varied between 20 and 100 ng m<sup>-3</sup> (standard deviation 20 – 130 ng m<sup>-3</sup>), while outdoor eBC mass concentration - from 340 to 990 ng m<sup>-3</sup> (standard deviation 170 - 660 ng m<sup>-3</sup>).

Keywords: Black carbon, aerosols, climate change, indoor air quality, I/O ratio

## **INTRODUCTION**

Black carbon (BC) has received particular attention around the world, not only for its impact on regional and global climate change but also on air quality and public health.[1][2]. Unfortunately, people in developed countries spend approximately 90% of their time in indoor environments (home, offices etc.) so exposure mostly occurs indoors, in homes, schools and workplaces. From which it follows that understanding the personal impact of PM<sub>2.5</sub> on a person requires a description of the fate and the transfer of PM of external origin to the internal environment[3]. Indoor concentrations of some pollutants have increased in recent decades due to such factors as energy-efficient building construction (when it lacks sufficient mechanical ventilation to ensure adequate air exchange)[4]. Existing evidence supports a positive association between indoor and outdoor aerosol black carbon mass concentrations and acute effects on human health and premature deaths[5][1]. Because of its finer size-mode (less than 2.5 µm), large specific surface area, and irregular morphology, BC can simply adsorb carcinogenic/mutagenic pollutants like polycyclic aromatic hydrocarbons (PAHs) and volatile organic compounds (VOCs) and can penetrate deep into the lungs, bloodstream and cause cardiovascular, ischemic heart disease, neurodevelopmental effects in infants and adverse birth outcomes, and respiratory morbidity and mortality due to chronic obstructive pulmonary disease, asthma, and lung cancer [1][6][7][8]. The effect of a 1 µg m<sup>-3</sup> increase in EBC on allcause mortality is at least eight times larger than the estimated effect of a 1 µg m<sup>-3</sup> increase in  $PM_{10}$ . World Health Organization report from 2012 concluded that "reduction in exposure to  $PM_{2.5}$  containing eBC and other combustion-related PM material for which eBC is an indirect indicator should lead to a reduction in the health effects associated with PM"[9]. Transport, especially with diesel engines, is the main source of eBC in urban areas. However, in some areas, residential combustion of wood or coal and at least occasional outdoor combustion of biomass may be even more important sources of eBC [10]. Based on the above, the main goal of this work is aimed at understanding the role of outdoor sources of emissions on indoor air quality in urban environments.

## METHODOLOGY

The study was performed at the Center for Physical Sciences and Technology at Vilnius, at urban region during the cold period (from October to December 2020). The building was built in 2016 and modern ventilation system was installed. eBC were measured in two places: (1) outdoor and (2) indoor (laboratory room). The indoor location was a vacant laboratory located on the 2nd floor near to other laboratories and offices which were used on every day during the study period. The studied laboratory had the same dimensions, geometry, windows and doors as the other laboratories in use, and was connected to them by means of a corridor. Doors and windows were always closed, except when people entered the premises to check equipment. In addition, air between laboratories was filtered by G4 type filters while air passing from outdoor was treated by G4, F7 and F9 filtering system. Equivalent black carbon (eBC) mass concentration was measured by using a Magee Scientific Company Aethalometer<sup>TM</sup>, Model AE31 Spectrum, manufactured by Aerosol d.o.o., Slovenia. The optical transmission of carbonaceous aerosol particles was measured sequentially at 7 wavelengths ( $\lambda$ = 370, 470, 520, 590, 660, 880 and 950 nm), where the eBC mass concentration was derived from the light absorption coefficient ( $\sigma_{ab}$ ) at 880 nm wavelength. All data was processed and evaluated. Weingartner correction was applied for values. The data points corresponding to invalid, extreme and missing values (zero or negative values) have been removed from the dataset. The flow rate of Aethalometer was set at 4,9 L min<sup>-1</sup>. Measurements were done with an interval of 5 min. In order to investigate indoor and outdoor air, a switch was installed which was changing from position indoor/outdoor occurred every 30 minutes. Instrument was operating in a way that no particles could be leaked to the laboratory.

### **RESULTS AND DISCUSSION**

# Investigation of weekly and diurnal variation of eBC mass concentration

On average, eBC levels were higher in the outdoor environment than indoors, with mean levels for the entire monitoring period of 50 ng m<sup>-3</sup> indoors, and 570 ng m<sup>-3</sup> outdoors. Mean indoor/outdoor (I/O) rations eBC for the entire monitoring period were 0.08. The indoor to outdoor (I/O) ratio are applied to evaluate the degree of penetration from outdoor to indoor. I/O ratio less than 1 indicates that the contribution of outdoor sources is greater than that of indoor sources. Fig. 1 indicates a moderate influence of outdoor eBC emissions on the indoor eBC level.



Fig. 1. Daily cycle of outdoor and indoor eBC mass concentration

The outdoor and indoor eBC concentration varied during the day. The highest level of outdoor eBC occurring in the rush hour period (from 7:00 to 11:00 and from 15:00 to 17:00 (GMT+2)) when people go to work and come back home, while the lowest level was found in the period of less traffic. The highest level for indoor eBC occurring in the period from 8:00 to 12:00 (GMT+2) when people came to work, which coincides with the morning peak for outdoor eBC mass concentration. The diurnal indoor eBC mass concentration varied between 20 and 100 ng m<sup>-3</sup> (standard deviation 23 – 130 ng m<sup>-3</sup>), while outdoor eBC mass concentration - from 340 to 990 ngm<sup>-3</sup> (standard deviation 170 – 660 ng m<sup>-3</sup>).

#### Statistical analysis of eBC mass concentration

Mean, minimum and maximum levels of BC at the indoor and outdoor locations are summarised in Table 1.

Weekday	Mean	Standart Deviation (SD)	Min	Median	Max
Monday					
Indoor	70	90	1	20	970
Outdoor	510	550	130	350	330
Tuesday					
Indoor	60	110	3	40	990
Outdoor	950	520	260	780	250
Wednesday					
Indoor	80	180	1	25	987
Outdoor	800	360	130	760	180
Thursday					
Indoor	40	80	1	20	690
Outdoor	650	290	180	590	140
Friday					
Indoor	40	80	1	20	750
Outdoor	550	250	130	520	130
Saturday					
Indoor	30	70	1	10	670
Outdoor	530	370	130	410	180
Sunday					
Indoor	30	60	1	12	470
Outdoor	400	200	130	360	180

Table 1. Statistical analysis of eBC mass concentration dynamics over the course of a week (ng m<sup>-3</sup>)

The weekend levels of eBC mass concentration were lower than in weekdays. The highest level of outdoor eBC mass concentration was observed on Tuesday and reached 950 ng m<sup>-3</sup> (standard deviation 520 ng m<sup>-3</sup>), while indoor eBC mass concentration was 80 ng m<sup>-3</sup> (standard deviation 180 ng m<sup>-3</sup>) on Wednesday. The lowest level of outdoor and indoor eBC mass concentration were observed on Sunday (in outdoor - 400 ng m<sup>-3</sup>, standard deviation 200 ng m<sup>-3</sup> and in indoor – 30 ng m<sup>-3</sup>, standard deviation 60 ng m<sup>-3</sup>). The results of this study demonstrate the variability eBC mass concentration associated with the characteristics of the measurement site, time of year and time of day, which is also reflected in earlier studies conducted in Finland and Spain [10][9]. The increasing outdoor eBC during the evening could be attributed to more wood burning related to residential heating and the homecoming traffic emission. Indoor peaks appear to be influenced in part by outdoor concentrations, as evidenced by the relation between average indoor and outdoor eBC daily cycles and indoor air movement associated with people coming to work.

# CONCLUSIONS

The article analyses the daily and weekly cycles of eBC mass concentration. The conclusions can be made as follows:

- Hourly mean mass concentrations of eBC for weekdays and weekends show diurnal cycles, which could be explained by periodicity of traffic intensity and heating activities. The highest level for the outdoor eBC is from 7:00 to 11:00 (from 380 to 690 ng m<sup>-3</sup>) and at 17:00 (990 ng m<sup>-3</sup>).
- The weekend levels of eBC mass concentration were lower than in weekdays for indoor and outdoor for 33% and 28% respectively.

• The results show that ventilation system affects indoor air quality, I/O ratios eBC for the entire monitoring period varied between 0.05 and 0.14.

Thus, a significant influence of outdoor air to indoor air was observed. This finding is crucial for offices located next to busy roads where outdoor eBC levels are higher.

### ACKNOWLEDGMENT

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# COMPARISON OF THERMAL OXIDATION AND PLASMA METHODS FOR AIR PURIFICATION FROM VOCS IN TERMS OF ENERGY EFFICIENCY AND ENVIRONMENTAL PERFORMANCE

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#### ABSTRACT

Volatile organic compounds (VOC) pose a serious hazard for human health and environment. These substances evaporate at ambient temperatures and can deplete the ozone layer. Generally, selection of VOC treatment technologies is based on removal efficiency and cost. The aim of this study is to carry out a comparative life cycle analysis (LCA) of Catalytic thermal oxidation (CTO) and Non-thermal plasma (NTP) methods applied for VOCs removal from flue gas stream. To carry out the life cycle analysis, the SimaPro 8.1 software (Ecoinvent 3 database) and the ReCiPe 2016 Midpoint method were used. In accordance with ISO 14040 standard, general LCA procedures have been performed. Both CTO and NTP technologies for cleaning gases from VOCs were modeled. The air purification process data for the LCA calculations (process inputs and outputs) were normalized for the capacity of the 1000 Nm<sup>3</sup> flue gas. The main focus was on the process of removing VOCs from the air in terms of energy consumption, emissions and environmental impact. The calculations revealed that NTP technology performed better than CTO from the environmental performance viewpoint with respect to categories: Ozone formation/Human health, Global warming, Terrestrial acidification, Stratospheric ozone depletion. The damage assessment in the Fine particulate matter category also highlighted the superiority of plasma purification processes over catalytic thermal oxidation.

Keywords: life cycle assessment, VOCs, non-thermal plasma, catalytic thermal oxidation

### **INTRODUCTION**

Volatile organic compounds (VOCs) are toxic and diffusive gases that can come from an array of sources, including human-made and natural sources. The major sources of man-made VOCs are: fossil fuels use and production (e. g. incompletely combusted fossil fuels or unintended evaporation of fuels); solvents used in coatings, paints, and inks; use of biofuel and biomass combustion. A significant source of indoor VOC emissions is, for example, the use of solvents in industrial processes involving the application of paints and varnishes to manufactured industrial products to protect the product from aggressive environmental influences. Emissions of VOCs are widely observed in construction and building sector, in household consumer products (detergents, etc.), and are also emitted from electronic devices [1,2]. In an enclosed space, such as a home, office or industrial area, these emitted VOCs accumulate and contaminate indoor air. In addition, high concentrations of indoor VOCs can lead to Sick Building Syndrome (SBS). SBS is a general term used to describe non-specific symptoms experienced by people in a building. SBS is directly related to the levels of indoor Total volatile organic compounds (TVOC) [3].

The most widely used and effective methods for cleaning exhaust gases from VOCs comprise: regenerative sorption, biological oxidation, thermal oxidation and chemical oxidation [4]. Modern technologies for cleaning exhaust ventilation using plasma methods are gaining popularity and can compete with traditional methods. Non-thermal plasma (NTP) methods are highly efficient in removing volatile organic compounds from exhaust gas stream. Purification using various technologies is usually associated with high energy costs. NTP method is one of the energy efficient methods of VOC purification [5, 6, 7].

Life Cycle Assessment (LCA) is based on internationally accepted standards and is widely recognized as the best approach to quantify the environmental impacts of a product (method) on the environment. Comparing the environmental impacts of alternatives solutions helps identify trends of development and provides insights in how to improve processes. Literature review revealed the lack of information on life cycle assessment of various VOC purification methods [8]. As a result, the aim of this study was to make comparative LCA analysis of Catalytic thermal oxidation (CTO) and Non-thermal plasma (NTP) methods for removal of VOCs from exhaust gas streams.

### PURIFICATION METHODS AND LIFE CYCLE ASSESSMENT

#### **Catalytic thermal oxidation**

The catalytic thermal oxidation (CTO) method is used to reduce the amount of industrial exhaust gases containing volatile organic compounds. Catalytic thermal oxidation offers several advantages (lower processing temperature, improved cleaning efficiency) over thermal oxidation, especially at low VOC concentrations. This system uses catalysts to speed up the oxidation process and lower the temperature in the combustion chamber. The use of catalysts makes it possible to reduce the temperature of catalytic thermal oxidation to 400-450 °C. This is almost half the temperature during recuperative thermal oxidation [9].

CTO works by raising the temperature of the exhaust stream to the point at which the chemical bonds holding VOC molecules together are broken (oxidized). VOCs from the process exhaust stream are converted to carbon dioxide ( $CO_2$ ), water ( $H_2O$ ) and thermal energy.

The process of catalytic thermal oxidation of VOCs operates at a lower temperature regime, which reduces fuel consumption and minimizes the formation of NOx. Reducing CO and NOx is very important because emissions of these compounds are regulated by environmental legislation.

#### Non-thermal plasma

Non-thermal plasma is one of the innovative ways to remove VOCs from the exhaust gas stream. Non-thermal atmospheric pressure plasma makes it possible to create active particles without generating excessive heat. The effective way of oxidizing organics is to use highly reactive species, i.e. reactants with a high oxidizing potential, such as -OH, -O, -H, O<sub>3</sub>, and H<sub>2</sub> O<sub>2</sub>. The hydroxyl radical is especially known to play an important role in oxidative purification and degradation of organic compounds. In non-thermal plasma, radicals, ions and other active species, which oxidize, reduce or decompose the pollutant molecules, are efficiently produced mainly via electron-impact dissociation, excitation and ionization of the background gas.

The molecules in the NTP reactor are activated by an electric field. In NTP, electrons are accelerated and active particles interact with VOC molecules, as a result, the oxidation process takes place [10]. During the oxidation process, VOCs are decomposed into more environment friendly compounds.

The use of non-thermal plasma pulsed corona discharge (PCD) has been reported in studies [11]. Experimental studies on the decomposition of VOCs using non-thermal plasma generated in a reactor with a dielectric barrier discharge (DBD) were published in [12]. In this study, the process of purification of ventilation exhaust using plasma was chosen as a typical installation (NTP reactor) [13, 14].

### Life cycle assessment

Life Cycle Assessment was used as a tool to investigate sustainability and quantify the environmental impact of the considered air purification technologies [15]. This study was carried out using life cycle assessment methodologies in accordance with the principles and guidelines of the International Organization for Standardization (ISO) in ISO 14040 and 14044 [16, 17].

Life cycle analysis was performed using SimaPro 8.1 software (Ecoinvent 3 database). The Ecoinvent database provides documented data on processes and products, helping to make the right choices regarding their environmental impact. In this study, the technological processes for exhaust gas treatment were set as system boundaries. The functional unit for comparison of two technologies was set as 1000 Nm<sup>3</sup> of treated flue gases. Energy consumption, emissions and disposal of by-products for the considered technologies were chosen as the main parameters. Materials for the production of treatment units, transportation and disposal were not assessed. This study did not include economic calculations and their impact on the considered purification technologies.

The data for inventory analysis of CTO treatment technology were based on publications [8, 18], while inventory data for NTP treatment were based on experiments performed at the Department of Environmental Technology, Kaunas University of Technology.

Parameter	Unit	Method			
		СТО	NTP		
Input pollutants VOCs	Kg	0.118	0.43		
Output pollutants VOCs	Kg	$2.35 \cdot 10^{-3}$	4.3.10-4		
Removal efficiency VOC	%	98.0	99.9		
Resources					
Electricity	klulh	2.84	0.32		
Gas (methan) Activated carbon material	m <sup>3</sup> Kg	9.83 - 7.10 <sup>-3</sup>	- 3.68·10 <sup>-6</sup>		
Catalyst (Mn-Co)	Kg	, 10	-		
Byproducts			2 52 12 5		
Activated carbon material	Kg	-	3.68.10-0		
Catalyst (Mn-CO)	Kg	$7.10^{-9}$	-		
$CO_2$	Ng Ka	20.03	0.333		
Water and Water vapor	мg	13.80	0.085		

Table	1.	The	inventory	analysis	data f	for V	OCs	removal	technol	ogies
I uoio	т.	THE	mventory	anarysis	uutu 1	.01 1	UC0	rennovui	teennor	USIUS

Damage assessment was carried out using the ReCiPe 2016 Midpoint method using the following indicators: Ozone formation – Human health Index (kg NOx eq.), Terrestrial acidification (kg SO<sub>2</sub> eq), Global warming (kg CO<sub>2</sub> eq.), Stratospheric ozone depletion (kg CFC11 eq.), and Fine particulate matter formation (kg PM2.5 eq).

# **RESULTS AND DISCUSSION**

The impact assessment by category is graphically presented in Fig. 1. The graphs show that the use of the catalytic thermal oxidation method for the removal of volatile organic compounds from gases has a greater impact on the environment and human health in all considered categories than the use of the NTP method.

In the category "Ozone formation, Human health" the greatest influence was indicated for CTO technology for the purification of waste gases from volatile organic compounds 2.54E-06 kg NOx eq., while for plasma technology - 3.03E-07 kg NOx eq., respectively. This can be



0.012

0.01

0.008

0.006

0.004

0.002

0

explained by the large consumption of natural gas and electricity in the technology of catalytic thermal oxidation of CTO (9.83 m<sup>3</sup> and 2.84 kW) in comparison to the NTP method.



0.0015126

92

NTP

сто

1.2E-09

1E-09

8E-10

6E-10

4E-10

2E-10

0

Soil acidification is characterized by a change in the chemical properties of the soil as a result of the deposition of nutrients (namely nitrogen and sulfur) in acidifying forms. Here we assess the environmental impact of sulfur dioxide (SO<sub>2</sub>). The Terrestrial acidification impact category encompassed by this ecological mechanism can also be attributed to the quality of the ecosystem. The effects of acidification are related to the atmospheric transport of released pollutants and their subsequent effects on soil pH, as well as the sensitivity of the ecosystem to soil acidity. The following damage results were obtained: CTO ( $4.02E-06 \text{ kg SO}_2 \text{ eq}$ ) and NTP ( $4.85E-07 \text{ kg SO}_2 \text{ eq}$ ).

The Global warming potential for the CTO method is much greater than for the NTP method. This is due to the fact that a significant amount of natural gas is used in catalytic thermal oxidation. Assessment of the Global Warming potential for the CTO and NTP methods showed the following results  $1.70E-02 \text{ kg CO}_2$  equivalent. and  $1.51E-03 \text{ kg CO}_2$  equivalent, respectively. This is due to the relatively low power consumption of the NTP method.

1.94703E-10

NTP

СТО

Emissions from combustion of auxiliary fuel (natural gas) also had an impact on the Global Warming category. This is due to the large volume of CO<sub>2</sub> emissions from methane combustion.

In the category of ozone depletion, CTO and NTP technologies contributed 1.69E-09 kg CFC-11 eq. and 1.43E-10 kg CFC-11 eq., respectively). The main source of influence was also the use of energy for cleaning gas emissions from VOCs. Natural gas has been a major source of ozone depletion. This is mainly due to the emissions of various chemical compounds during the extraction, transportation and use of natural gas.

Fine particulate matter (PM2.5) pose the greatest danger to human health and the environment. These small particles can travel deep into the lungs and even into the bloodstream. In addition, an increase in the amount of particulate matter in the air can cause changes in surface temperature, an increase in solar radiation, which leads to serious consequences for the climate.



Fig. 2. Damage assessment in category Fine particulate matter formation

As shown in Fig. 2, damage assessment in category Fine particulate matter formation for the CTO method was 1.85E-06 kg PM2.5 eq., it is more than using the NTP method 2.23E-07 kg PM2.5 eq. This is due to the large amount of formation of fine particles during the combustion of auxiliary fuel.

The results of calculations are comparable to such calculations of other studies [8, 15, 18]. The difference between the values obtained other studies in this area can be explained by the use of various methods (Impact 2002+, EPC 2000, ReCiPe, etc.) and also use various data sources (Ecoinvent, Gabi, ProBas, etc) for the calculations of LCA. Due to the complexity of LCA analysis, (search for inventory data) during calculations use various system boundaries. These system boundaries will have a direct impact on the final result of the calculations.

Based on the results obtained using the ReCiPe method, it was shown that plasma (corona discharge) technologies for removing pollutants (in this case, volatile organic compounds) are more environmentally friendly than technologies for catalytic thermal oxidation.

Comparison of NTP and CTO technologies showed that the use of thermal catalytic oxidation technology for VOCs removal is more harmful to the environment than the use of non-thermal plasma. This is due to the amount of energy required to remove VOCs from the same volume of the exhaust ventilation. Electricity consumption and especially the use of auxiliary fuels (natural gas) had the greatest impact on all impact categories.

Comparative characteristics of life cycle assessment of the considered methods for removing volatile organic compounds from waste gases showed that NTP technology offers a more environmentally friendly alternative compared to catalytic thermal oxidation.

### CONCLUSION

Research using the NTP method shows that the use of non-thermal plasma for air purification has the lowest overall environmental impact than catalytic thermal oxidation. The great damage from the use of the catalytic thermal oxidation method is mainly associated with the use of gas in the thermal treatment of VOCs (extraction, transportation, use of additional equipment, formation of by-products during combustion, etc.).

The NTP method has the advantage mainly of lower energy use for cleaning  $1 \text{ m}^3$  of contaminated gas. When using energy from other sources (for example, renewable), these values can be even lower. The method of non-thermal plasma air purification from volatile organic compounds showed the best results in terms of impact on the environment. This method can be recommended for further use in air purification from VOCs, since it is more environmentally friendly.

A comparative environmental assessment of the process of cleaning polluted air from volatile organic compounds using various technologies was carried out. The results of the life cycle analysis showed that, within the framework of the studied boundary system, the plasma treatment of the exhaust gas air stream of the exhaust ventilation works better than the thermal catalytic oxidation technology in terms of environmental damage.

In general, plasma technologies have proved to be competitive and more preferable than thermal catalytic oxidation. The lower amount of electricity, as well as the lack of the need to use natural gas, necessary for cleaning exhaust gases from ventilation, indicates that plasma technologies can be recommended as more efficient in terms of energy efficiency, as well as more environmentally friendly.

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# THE ROLE OF GLOBAL EDUCATION IN SUSTAINABLE ECONOMY

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### ABSTRACT

The 17 "Sustainable Development Goals" (SDGs) were adopted by the 193 member states of the United Nations in September 2015. They are an advanced development of the Millennium Development Goals (MDGs), which adjourned in 2015.

The "Sustainable Development Goals" are a large–scale, holistic and long–term set of goals. They are the universal agenda that require perpetual domestic and international progress. In addition, they require both an endeavour on the governmental and social levels.

"Global Education Goals" render the corresponding aims: by 2030 ensure that all participants acquire essential knowledge and skills to promote sustainable development, including among others through education for sustainable development and sustainable lifestyles, human rights, gender equality, promotion of cultural peace, global citizenship, and appreciation of cultural diversity and cultural contribution to the sustainable development.

The objective of this research is to develop and enhance Global Education within a sustainable economy.

The key aim and result is the development of Global Education as an active learning process that enables people to get acquainted and enhance their knowledge of the international priorities and principles of the sustainable development, to identify the causes and impacts of global changes and challenges, and to promote personal engagement and informed decision—making process. Developmental education is based on the principles of solidarity, equality, inclusion and cooperation. The concept of sustainable development is based on the need to optimize economic development and social system, as well as the impact on the environment and usage of resources. This development model should ensure the sustainability in time and space of the economy, the environment and the social field.

The theoretical research methods, analysis of literature, documents, legislation, information obtained on the internet and graphic analysis were used throughout the research.

**Keywords:** sustainable development, global education, international development, global challenges, sustainable economy, global health

# **INTRODUCTION**

Globalization is challenging to define as it is a dynamic phenomenon. According to the report of the World Commission on the Social Dimension of Globalization, the key characteristics of globalization are "The liberalization of international trade and the emergence of massive cross-border financial flows". While describing the consequences of globalization, the report states: this resulted in increased competition in global markets. It is also widely acknowledged that this has come about through the combined effect of two underlying factors: policy decisions to reduce national barriers to international economic transactions and the impact of new technology, especially in the sphere of information and communications.

Globalization is essentially defined through the lens of global economic development but it undoubtedly has broader institutional and social ramifications. It is more than a particularly advanced state of cross-border economic interdependence and can be viewed as a process of progressive interdependence driven by factors that bring societies and citizens closer together, in fact by policies, institutions and private initiatives that support the integration of economies and countries.

It is therefore necessary to examine to what extent imbalances brought about by globalization call for better institutional frameworks and policies. Just as it is arguable that most of the social gains for the Western industrialized societies occurred as a consequence of the social regulation of industrialization while it is equally plausible that labour issues should properly be addressed through a similar process of social regulation of globalization. More specifically, one should ask whether new regulatory modes and mechanisms such as hard and soft law, labelling, and public and private codes of conduct-or institutions need to be pursued in comparison to traditional international labour laws.

This question arises from positive and negative aspects. On the positive side, the phenomenon of globalization promotes transnationalism in labour-standard setting. For some scholars, the national labour law can at most be considered a local and thus increasingly relative, if not insufficient response to phenomena of global change. On the negative side, while the economy is becoming increasingly global, social and political institutions are still mainly local or national.

### **GLOBAL EDUCATION CONTEXT**

The 17 "Sustainable Development Goals" (SDGs) were adopted by the 193 member states of the United Nations in September 2015. They are a further development of the Millennium Development Goals (MDGs), which ended in 2015 and they differ from the MDGs in a number of significant ways. The goals and targets comprising the SDGs are intended to be universally valid and aim to achieve a holistic development with equal value within the sustainability. In addition to this, the SDGs break new ground by demanding that the countries of the global North should be implementing the goals based on the belief that only through the genuine participation of the developed and industrialised world would it be possible to end poverty, protect the planet and ensure prosperity and a life with dignity for all.

The Sustainable Development Goals are large, holistic and a long-term set of goals. They are a universal agenda, requiring progress at home and world-wide and require an entire society endeavour.

According to Werner Case (1997), movements to promote a global perspective within social studies are due to the state of the planet as a whole and an understanding of how its systems-political, cultural, econimic, ecological, and technological-are linked and

how these are manifested in relationships. Werner & Case (1997) introduce the importance of differing perspectives by stating "global education has been associated with curriculum reform advocating a more global perspective on the world. A need exists for students to examine the world from varying perspectives and to become aware of the complex interrelationships that characterize it." [1]

Hicks (2003) further explains that each of these four elements needs to be present before one can claim to be involved in global education. Both Selby & Pike have written extensively on the importance of ecological thinking in global education and this is evident within the four-dimensional model that they propose for global education. It needs to be stressed that the environmental health of the world is just as important as taking care of all humanity and that the two must work together simultaneously. For example, when explaining the spatial dimension Selby (1998) writes that "this dimension also concerns the cycles and systems of nature and the relationships between human society and the environment.[1]

#### National strategies on Global and Development Education.

The Education 2030 Agenda, which originated from the World Education Forum (WEF) 2015 held in Incheon, Republic of Korea (UNESCO, 2015a; United Nations, 2015), positions education as one of the fundamental tools for the sustainable, inclusive, fair and cohesive development of a country. In particular, the concepts of inclusion and equity are visualized as the foundations of systemic approach to assure educational quality (Marope, 2014) within a transformational, humanistic and holistic vision of education, which will contribute to the improvement of the lives of individuals, families, communities and countries.

Essentially, inclusion entails responding effectively to context-inequalities and ensuring personalized learning opportunities that are relevant to the diverse expectations and needs of all learners (IBE-UNESCO, 2016). Equity, on the other hand, focuses on guaranteeing that fair educational conditions, inputs and processes pave the way to equality in learning outcomes for all learners (López, 2005; Opertti, 2017). [11]

This section will remit the Czech National Strategy on Global Development Education, the Austrian strategy on Global Learning and the Spanish, the Irish and the Portuguese evaluations of their Development Education strategies.

#### Austria

The development of the Austrian Strategy for Global Learning was the result of a multiannual process. It was informed by the European discourse and embedded in the European strategy for the strengthening of Global Education and Learning in European countries, as formulated in the Maastricht Declaration (2002). During the development of the Austrian strategy, experiences of similar processes in Finland and Ireland emerged.

The strategy that was developed with aims to make Global Learning widely recognised within the Austrian education landscape and to strengthen it by the following measures:

Strengthening the structures of Global Learning in the Austrian formal education system, especially in the areas in-service training of teachers, teacher training, school development, curriculum development, external Global Learning programmes and the educational materials for schools and pedagogy.

Widening academic lecturing and research in Global Learning as well by promoting a process of reflection on theory and practice of Global Learning; especially by offering a wider range of courses and lectures on Global learning at Austrian universities.

Implementing the research projects and promoting publications on Global Learning.

Developing the further concept of Global Learning, Strengthening Global Learning in the non-formal education sector, especially in adult education

Establishing a commitment to Global Learning with various actors and stakeholders.

### **Czech Republic**

After the first Czech Strategy on Global Development Education has been implemented between 2011 and 2015, there was a necessity to look back at its achievements and benefits, but with its limitations. For the first time, the strategy defined the main goals of Global Development Education (GDE) within its topics, principles, target groups and stakeholder involvement. It aimed to integrate GDE into formal education at all levels, to support awareness-raising, develop co-operation and partnership, to ensure financing and to increase the quality and effectiveness of GDE programmes. The strategy's vision was to reduce the gap in the field of GDE between the Czech Republic and Western European countries by 2015.

There were a number of successes and positive outcomes of the first strategy on GDE in the Czech Republic. One of the main successes of the strategy that it increased awareness of GDE in the education system overall. [9]

### Ireland

The consultation for the Irish Aid Development Education Strategy took place in partnership with individuals and organisations across the formal and non-formal education sectors in Ireland, in line with Irish Aids work in the Development Education. Partnership is a core value of the Irish Aidas as it is believed to increase the accessibility, quality and effectiveness of the Development Education in Ireland.

The Irish Aid Development Education Strategy 2017-2023 is the product of a collaborative and wide-ranging engagement process with a variety of stakeholders including the government departments, state agencies and the development education partners.

### Portugal

A team at the Faculty of Psychology and Education Science at the University of Porto was selected by the Development Education Strategy Group to carry out the evaluation of the National Strategy for Development Education 2010-2015. The process was oriented towards learning and accountability and it reinforced the promotion of the culture of evaluation, innovation, diversity and history.

### Spain

The purpose of the Development Education Strategy paper (2008) was to facilitate the creation of a development cooperation policy and a society committed to sustainable human development, along with the eradication of poverty. The Master Plan for the Development Cooperation (2005-2008) recognised the significance of Development Education (DE) and identified it as one of its intervention criteria for achieving the objectives set out by the international community.[9]

### **Global Education institutions in the Baltic countries**

### Latvia

There is no separate, official legislation covering GE at schools. Projects implemented by NGOs are a significant source for incorporating GE issues into formal education. A project entitled Global Dimension in the Subjects of Social Sciences in Formal Education implemented by the Education Development centre was one of the most visible projects. The overall aim of the project was to integrate GE themes across the curricula of social science subjects and into the formal education system; an in-depth analysis has been carried out on the GE dimensions in the Latvian education system and in other European countries with the aim of developing methodologies for teachers. These are the first GE guidelines of this kind that can be used by teachers, students and representatives of NGOs working with GE.

"Critical thinking in the teaching/learning and educational process for promoting the society's awareness of diversity and integration" was another programme in Latvia. It dealt with issues such as global citizenship, international processes, globalisation, migration, local action for global changes, sustainable lifestyle, diversity in the society, and intercultural communication.

# Lithuania

As part of the Global Action Week, the Lithuanian Ministry of Education and Science and the Lithuanian Children and Youth Centre met at the national level to discuss formal and non-formal education for teachers. The agenda included the organization of creative educational, artistic and experimental workshops and contests. Governmental, non-governmental and private educational institutions had an opportunity to present innovative educational activities.

### Estonia

Themes related to Global Education (fair trade, global environmental problems, democracy, developing countries) are included in various subjects, predominantly in civics, history and geography courses. There is an optional course "Globalizing World" in the upper-secondary school.

The projects by NGOs are the main activities of integration global development issues within formal education. NGO Mondo is the leading organisation within the field of Global Education in Estonia.

# **GLOBAL EDUCATION AND SUSTAINABLE DEVELOPMENT**

While planning, implementing and evaluating sustainability of development, several basic principles have been developed. One of these is the socio-ecological principles that clearly illustrate the regularities of the development process, thus enabling the precise definition of the developmental goals.

Transition paths to sustainable development can be diverse and it is easy to make mistakes, but a clear definition of a goal is a prerequisite for development. The advantages of socio-ecological principles are that they value sustainable development from the system's point of view and they consider actions in a series from the very beginning.

In a sustainable development, there are four key sustainability aspects that respond to the question "How to do that", to ensure social development.[2]

1. **Diversity** is a prerequisite for the further development of any system (including society). Biodiversity, economic diversity, and cultural diversity are fundamental to biosphere and society to maintain their dynamic stability. Innovation and adaptation to new circumstances are possible if there are different approaches and development alternatives from which it is possible to build new, stable public systems. Diversification is often the most appropriate strategy to increase the long-term stability.

2. **Subsidiarity** remits all kinds of functions at the lowest possible level of administration. Assistance or guidance from outside is only desirable if it contributes to the performance of the delegated function in question but at the same time does not seriously reduce the autonomy of the subsystem. Self-government is closely linked to social responsibility and social security and can be used in all areas such as – politics, administration, business, technical systems, ensuring economic material flows. This principle does not provide clear

guidance, but requires an optimum solution between autonomy and integration in wider systems. Introducing the principle of self-determination promotes the involvement of individuals and the activity of local governments to create and manage their lives while promoting democracy.

3. **The principle of cooperation** emphasizes the significance of horizontal and nonhierarchical interactions. Such a collaborative model is based on common goals and laws and is usually open where the participants can either join or withdraw. Networks of cooperation provide an exchange of experience and information, create mutual support, stabilize systems and promote competition – participants can choose a more attractive network. Therefore, the ability to adapt to the new and focus on the needs of participants is vital to the existence of networks of cooperation.

4. The **participation** or **principle of participation** corresponds to the ideas of democracy and is the basis for various approaches. This is vital in order to avoid conflicts. In particular, the significance of the participation of all parties involved in the resolution of the problem in the initial stage of the formulation of the problem and the identification of possible alternatives. Participation promotes responsibility and motivates people to contribute to the implementation of a specific decision. In addition, participation requires the time and interest of the participants, the openness of the institution involved, and often additional time and resources than well-designed hierarchical decision-making. The choice of procedure requires the understanding of a risk that the decision may not correspond to the opinion of the experts, but the principle of participation requires respect for different interests and opinions.[2]

While the basic principles of sustainable development are diverse, the use of specific basic principles makes the decision-making of important economic, political and environmental protection decisions more practical. When assessing the implementation of sustainable development, the question of the use of the concept of sustainable development for countries with different economic and social regimes is particularly important.

So far, the opportunities for sustainable development have been studied most extensively for industrialized countries. Although the number of these countries is relatively small, respect for the basic principles of sustainable development in them is particularly relevant in the context of the high level of consumption, which is one of the main causes of problems in the free market economy and globalization processes.

The situation in industrialized countries is quite different in comparison to the situation in Africa, most Asian and South American countries, also many European countries. The people's desires of these countries to reach the level of prosperity of industrialized countries as soon as possible further emphasizes the need to achieve decoupling of economic development and material consumption.

On the other hand, in the poorer countries of the world, the issues of sustainable development are related to the problem solving of the free market economy and the negative consequences of globalization, which is essentially impossible at the local level.[3]

# ENVIRONMENTAL PROBLEMS AND SOLUTIONS

The planet faces a variety of troubling issues that stem from non-made contamination. This leads to environmental problems that are causing long term damage to the earth's ecosystem. The Global Issues website explains that the only way to control current environmental issues is to create sustainable development strategies and continue to instill conservation methods. Some manmade accidents threaten wildlife and the ecosystem. Although these accidents are relatively rare due to increased safety procedures, nevertheless

accidents still occur and sometimes with devastating effects. Such examples of accidents include oil spills, radioactive leaks, tanker spills, pipeline bursts and drilling accidents. The best solution for accidental spills and leaks is to create additional safety protocol using both computerized and human detection systems.

Water pollution is a growing problem globally. According to the Thinkquest website, large industries including those that produce chemicals and plastics dump a large amount of waste into the water. Human waste and rubbish also end up in the oceans and lakes. The Clean Water Act of 1972 allows the U.S. government to enforce restrictions on those who dump trash and waste. To address the problem, individuals can improve recycling and waste disposal and they can volunteer to clean up shorelines and nearby public locations. Businesses should develop ongoing protocols to reduce the amount of chemicals and other waste they dispose into the water supply.[10]

The United Nations Environment Program (UNEP) can provide an international forum to promote the idea of "green" concrete and what our industries can do for the environment. This would give the supporters of the Global Economy an opportunity to prove their commitment to the environment protection. [7]

### POLITICAL CONTEXT AND CHALLENGES

Among the European ministries, agencies and other bodies with national responsibility for the Global Education policy, strategy and funding, the following cross-cutting challenges featured prominently at the macro-political level in 2016:

- Refugees coming into Europe, primarily from the war
- The rise of right-wing political parties

These themes featured not only in the country reports submitted to GENE during 2016, but also during the GENE conference in Paris organised in collaboration with the French Ministry of Foreign and European Affairs and the French Development Agency in November 2016. The primary aim of this Global Education conference was to bring together the GENE network with civil society organisations and local and regional authorities to consider the current challenges facing Europe and the world, as well as the opportunities for Global Education to play a role in addressing them. [9]

### **Refugees coming into Europe**

Many countries in southern Europe are dealing with increased numbers of immigrants and refugees either fleeing war-torn countries in neighbouring regions, or fleeing poverty in search of better lives in Europe. Greece, Italy, Malta and Cyprus report that they are continuing to receive increased numbers of people, and numerous number of children. Many other countries throughout Europe, including Germany, Sweden and Norway, have also welcomed significant numbers of refugees. This presents challenges for national education systems both in terms of needing to cater to higher numbers of students from diverse backgrounds, and also in terms of being able to adequately address the educational needs of children who have experienced recent trauma and who often do not speak the local languages.

Right-wing political parties continued to rise in popularity across Europe in the last few years and gaining significant proportions of the popular vote in Austria, Finland, France, Germany, Greece, Hungary, Netherlands, Poland and Sweden. The rise of the right-wing parties has been accompanied in different countries by increasing anti-immigration sentiments and rhetoric, ethno-nationalist ideologies and euro-scepticism, as well as by antielitist, anti-globalisation discourse on the back of rising unemployment and political disenfranchisement.[9]

### **Global Health**

COVID-19 has not yet disappeared, and some voices are already warning about a more virulent new outbreak of the virus that will strain even more, if possible, the health systems of most countries, but especially the more vulnerable, whether it be COVID-19 and other diseases international society has begun to accept the idea that the world we live in has changed, and such international agreements as the 2030. Agenda are at risk. Experts, politicians and other actors are currently identifying how and where that change is taking place and how it will affect global balance and the positioning of individual states in the international arena.

With these ideas in mind, our study pursues two objectives; first, to shed some light on how the COVID-19 pandemic could affect the behaviour of individual actors and threaten their commitments to international cooperation, jeopardizing the implementation of the 2030 Agenda and the achievement of Global Health for all; second to analyse how the institutional design of the 2030 Agenda could be affected by the COVID-19 crisis and how it should be adapted in consequence, according to the experts view.[12]

# **GLOBAL EDUCATION REQUIRES INNOVATION AND CREATIVITY**

The Development Education Research Centre (DERC) is a part Institute of Education and is one of the world's leading centres for development education, global learning and global citizenship. Its main objectives are to promote the value of development education as part of essential learning in the twenty-first century and to develop an international community of researchers engaged. GE is gradually developing a body of evidence through a series of published monographs, academic articles and seminars on relevant themes, organising teacher training, educational courses and other initiatives on such relevant topics.[9]

When analysing the explanation of innovation concept as it has been presented in the work of different worldwide scientists, as well as in normative documents of the European Union, OECD (Organisation for Economic Co-operation and Development) and Latvia, it can be concluded that they render contrasting views and goals. There is a common viewpoint that a more rapid development will be observed only in those countries where innovation is among the most important political and economical priorities. One of the essential differences regarding the explanation of the term is connected with different approaches. This includes two approaches:

• innovation as creative process;

• innovation as technological process of novelty introduction which results in the development of new goods, services and production technologies.

In Latvia the term innovation has been defined in numerous documents. The law of scientific activity introduces the following definition: *innovation* – the implementation of a new scientific, technical, social, cultural or another kind of ideas, elaborations and technologies within the form of a product or service. Within the framework of Latvian long-term development strategy till 2030 "innovation" has been explained as a process during which new scientific, technical, social, cultural and another kind of ideas, elaborations and technologies are implemented in the form of competitive and marketable products or services [11].

## **Scientific Technological Innovation**

In the context of the European Union countries there exists a considerable significance of scientific technological innovation by incorporating eight kinds of activities:

1. Research and development of technologies (R&D) – systemic creative work to increase the fund of knowledge, including human, social and cultural knowledge, with the aim to use the fund for the development of new ideas. R&D incorporates the development of fundamental research, applied research and technologies.

*Fundamental research* is an experimental or theoretical work carried out in order to gain new knowledge regarding some observed phenomenon or fact. The kind of research is connected with the analysis of characteristics, structures and relationships with the aim to formulate and test the hypothesis, theories and rules. Usually the results of the fundamental research are not sold, but published in scientific periodicals and offered to interested colleagues instead.

*Applied research* is the investigation of original research in order to gain and develop new knowledge. It is aimed at the achievement of previously set *practical* aims.

*Development of technologies* incorporates systematic work based on the existing knowledge gained from previous studies and practical experience and aimed at the production of new materials, products and equipment, the introduction of new processes, systems and services, or considerable improvement of the existent goods, services and processes.

2. Acquisition of nonmaterial technologies – the discovery of patents, unpatented inventions, licences and *know-how*, obtaining of trademarks, drafts, software, and the like, in connection with the implementation of innovation.

3. Acquisition of material technologies – equipment with technological improvements connected with the innovation of product or process implemented by an enterprise.

4. Industrial engineering – changes in production equipment, process of production, mechanism and standards of quality control necessary for the production of new products and introduction of new processes.

5. Pre-production activities – modification of products or processes, retraining of employees, pilot production.

6. Marketing of new products – research of the market, adoption of products to fit in the market, preparation of advertisement, a. o.

7. Designing work – plans, drafts, drawings necessary for the defining of procedures, technical and operational descriptions in order to facilitate the preparation, development, production and marketing of new products and processes.

8. Acquisition of other kinds of capital – buildings, equipment and tools without any technological improvement necessary for the creation of new or advanced products or processes.[1]

## **Innovation Process**

Schematically innovation process can be depicted either as a linear or nonlinear model



Figure 1 Linear model of innovation process.

Linear model of innovation process is depicted in Figure 1. In accordance with linear models innovation process can be conceived as the one-way flow of information without any feed-back, activities, and often it has an occasional feature.

In the age of globalization, high technologies and information revolution successful commercialization of knowledge within a company, branch or country is possible only if innovation process agrees with nonlinear model (Figure 2). On the one hand, the occasional feature of activities in it has been minimized, while planning is in process. On the other hand, the flow of information obtains forked and feed-back oriented activity. For example, the orders of clients (consumers) directly reach producers or scientists and university lecturers, thus science and authorities of higher education are connected with production and the interests of consumers. In the nonlinear model, the processes are simultaneous and happen through interaction, which means constant cooperation between scientists and market (client, consumer, customer). On the contrary, in the linear model there is no such interaction between the activities and the next activity begins only after the previous one has ended, which is not likely to conform with the real situation of free market [7].



Figure 2 Nonlinear model of innovation process

Innovation process comprises several branches and spheres of the national economy. Successful implementation of the process cannot be conceived without the cooperation between its participants and coordination of priorities (the system of aims and objectives), as well as clear rules of activity and sound financial base.

### **Innovation System**

Worldwide practice testifies that in order to successfully implement innovative activities there are being formed within the national innovation systems (NIS), where the interaction between innovative companies, education – science system, government and financial system emerge. Innovation can be discussed as a national system only if it comprises:

- higher education and science;
- business;
- financial system for supporting innovations;
- legislation favourable for innovation.

In order to secure successful functioning of NIS, its components must be compatible with the following features:

• at universities there is being carried out fundamental research at global level, giving students a chance to become competitive and recognized higher education; national and private establishments of elementary and professional education produce qualified professionals with the necessary skills and knowledge suitable for certain scientifically ample branches.

• industrial section (basically private) is able to invest in innovative activities and give up to 80% financing to national research (form the total research and development financing – R&D of the country);

• government creates an innovation-friendly environment by adapting favourable credit policy, tax and customs policy, as well as investment policy, so that the financing of R&D activity would be favourable for the private section;

Global experience testifies that within the context of the economic tendencies' analysis and national politics the concept of innovative company refers to the performer of the technological innovations (i.e. the creator of new or considerably improved products and/or processes) in accordance with the definition of the term ''technological innovation'' stated in the manuals of OECD Oslo and Frascati. [7]

# CONCLUSIONS

1. The important trend is the globalization and diversification of emerging markets. If we look back a decade, most of the innovation in PR was designed in New York and London. Since then we have witnessed a growing diversity of innovation. The Nordic countries, New Zealand and other creative hot spots in Asia provide classical examples. China is leading the way in PRs content to commerce revolution based on the remarkable WeChat platform.

2. Since the early 2000's the PR industry has undergone very rapid change with accompanying structural changes in the business model under which it operates. The principal driving forces behind these changes have been the growth and popularity of global social media platforms and other significant technological innovations.

3. Social Media platforms is a vital role in Global Education (which reminds us regarding the relatively recent grand scheme; Facebook (2004), YouTube (2005), Twitter (2006). Facebook in particular has recently been feeling the heat on this issue, but it is the dominant use for all of us. How to use the insights that data bring while balancing this with the need to retain people's trust and engagement. Breaching privacy is one potential threat to that trust. In the EU, that is now a clear legal issue as its new GDPR legislation has come into effect aimed at protecting the privacy of the EU citizens.

5. Global Education portrays a shift on the continent toward a willingness by actors representing different strands of Global Education to come together, despite their differences, origins and schools of thought and by growing interagency, inter-departmental and interministerial cooperation.

6. Global Education Network Europe has been addressed to the policy situation in Europe. Policy learning, cohesion and better policy solutions can be attained by sharing our diverse approaches and knowledge and by bringing our experiences together in practical ways.

7. Environmental problems and solutions are important roles in Global Education. Water pollution is a growing problem globally. According to the Thinkquest website, large industries including those that make chemicals and plastics dispose a large amount of waste into the water. Human waste and rubbish also ends up in the oceans and lakes. The Clean Water Act of 1972 allows the U.S. government to enforce restrictions and those who dump trash and waste.

8. It is widely accepted that the 2030 Agenda requires a global partnership for its implementation where not only governments, but also the private sector, civil society organizations, international organizations and other actors are summoned to participate.

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# THE GENOTOXIC IMPACT TO PERIPHERAL BLOOD CELLS IN PERCA FLUVIATILIS INDUCED BY MULTIPLE STRESSORS

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### ABSTRACT

Increasing pollution in aquatic systems is causing damage to living organisms. Moreover, aquatic animals are constantly infected with various parasites. These parasitic infections may violate host animal (i. e. fish) immune system in this way weakening its resistance to various pollutants (i. e. heavy metals). Therefore, this study focuses on genotoxic damage to Perca fluviatilis peripheral blood cells caused by co-infection with protozoan parasite of fish Trichodina sp. and pathogenic oomycete Saprolegnia parasitica combining it with metal induced chemical stress. These stressors, whether it occurred naturally or was caused anthropogenically, can lead to unpredictable genotoxic outcomes in aquatic organisms, especially if they befall simultaneously. Until now, there have been no studies covering combined effects induced by parasitic co-infection and metal mixture exposure on genotoxicity in fish. Thereupon, the analysis of nuclear abnormalities, including micronucleus (MN), nuclear buds (NB) and blebbed nuclei (BL) in erythrocytes of peripheral blood cells was performed. The experimental study was focused on recreating realistic interaction conditions concerning multiple stress effects. The research results show that simultaneously co-infected and exposed to pollutants fish tend to receive highest genotoxic impact compared to that when only one stressor appears. This study also proposes that stressors (parasites and metals) may affect fish in synergetic manner, both generating genotoxic damage to organism and not mitigating one another's effects.

Keywords: genotoxicity, water pollution, fish blood cells

### **INTRODUCTION**

Increasing pressure from human activities is causing a variety of environmental problems. One of them is pollution. Pollution causes versatile damage to all ecosystems. Aquatic systems are no exception. Living organisms are being constantly exposed to several types of pollutants that cause stress [1], [2], [3]. Overall, the most common stressors are pathogens and xenobiotics [4]. On the other hand, animal (i. e. fish) infections with different parasites are quite natural and common in aquatic ecosystems [5]. Therefore, aquatic animals are simultaneously exposed to different types of stressors derived from both natural and anthropogenic sources. Besides, coinfections or mixed infections may occur when host becomes infected with several different pathogens (simultaneously or secondary) which can cause unique effects on animal. In this way, pathogens alter organism's immune response to one another and also to pollutants. The magnitude of this effect can cause positive or negative impacts on the host. Therefore, hostpathogen interactions may vary in polluted habitats, and the adverse effects of these interactions are unpredictable. In one way, pathogens may increase or decrease host susceptibility to other types of stressors (i. e. metals). In another way, anthropogenic stressors may decrease pathogen's activity. Also, one pathogen may alter the severity and course of a disease caused by another stressor. Mixed infections may also cause additional stress on their host susceptibility to pollutants and in the case of monospecific infections, these effects may vary [6]. In naturally occurring conditions, most animals are exposed to a mixture of contaminants and are simultaneously infected with multiple parasite species. Therefore, more multiplestressor studies are required to predict the effects of stressors interactions on aquatic biota,

which can then be used to improve models for assessing cumulative risks. Thus, in this research, we examine how co-infection of *Trichodina sp.* and *Saprolegnia parasitica* affects susceptibility of host fish *Perca fluviatilis* to genotoxic agents such as metal mixture.

# **METHODS**

### **Study animals**

Fifty healthy and naturally infected individuals of *Perca fluviatilis* were collected from various ponds at a fish farm (Kaišiadorys Dictrict, Lithuania). For acclimatization, the fish were kept in holding tanks supplied with flow-through aerated deep well water in optimal physicochemical conditions for two weeks under natural light cycle conditions and were daily fed with red worms (*Eisenia fetida*). During the experiment, both the water and diet were kept unaltered.

### **Parasites**

# Trichodina sp.

Fish were externally examined for naturally occurring ectoparasites. Trichodinids were identified, no mixed infestation by other parasite taxa was observed. After the examination, the specimens of *P. fluviatilis* infected with trichodinid parasites were selected for a multiple stress exposure experiment.

# Saprolegnia parasitica

Pure living cultures of *Saprolegnia parasitica* Coker were isolated from naturally infected fish. *S. parasitica* was experimentally transmitted to the fish infected with *Trichodina sp.* 

# Metal mixture solutions

To prepare metal mixture solutions the certified standard single-element metal solutions  $(Ni^{2+}, Cd^{2+}, Cu^{2+} \text{ and } Pb^{2+} 1000 \text{ mg/L in HNO}_3 0.5 \text{ mol/L (Certipur®, Germany), and Zn^{2+} 10 000 \text{ mg/L in 5% HNO}_3 (Roti® Star, Germany), respectively) were used. For Cr, the analytical grade K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> was dissolved in distilled water to prepare stock solutions of 1000 mg/L. Using a volumetric flask, a certain volume of each metal (Cr, Cd, Ni, Cu and Zn, respectively) from the stock solution was diluted in 1000 mL of distilled water with 0.1 M nitric acid. The influence of water hardness on real concentrations of metal ions was tested. Taking into account water hardness, metal mixture solutions were prepared in which the concentration of each metal was 1.5-3 times higher than its normal value. In the HDPE bottle one day before the test initiation, the stock solution was prepared to allow for chemical equilibration. Table 1 shows that measured metal concentrations of MIX corresponded to nominal metal concentrations at maximum permissible concentrations (MPC) for inland waters in the European Union (Directive 2008/105/EC) [7]. During test without fish, to identify the possible contamination by and/or sorption of metals in tanks, the designed nominal metal concentrations in the tans were checked. With time, no significant changes in metal concentrations were observed.$ 

Metal	MIX* Nominal concentrations	MIX Measured concentrations
$Cd^{2+}$	0.0015	0.0012
$Cu^{2+}$	0.0100	0.0090
Cr <sup>total</sup>	0.0100	0.0120
$Pb^{2+}$	0.0140	0.0090
Ni <sup>2+</sup>	0.0340	0.0290
$Zn^{2+}$	0.1000	0.1150

Table 1. Values of nominal and measured concentrations (mg/L) of metals in the complex mixture solution

\*maximum permissible concentrations (MPC) for inland waters in EU (Directive 2008/105/EC).

## The experiment

The experiment was conducted under semi-static rotating water-current conditions on the fish which were divided into 4 groups, depending on the stress type to which they were exposed: a) control, b) single chemical stress, c) co-infection and d) multiple stress. For multiple stress conditions, the fish were co-infected with two parasites (Trichodina sp. (naturally) and S. parasitica (experimentally)) and exposed to a chemical mixture (metal mixture). The uninfected and infected fish were exposed to metal (Cd, Cu, Cr, Pb, Ni and Zn) mixture (hereinafter referred to as MIX) at the concentration corresponding to Maximum-Permissible-Concentrations (MPC) accepted for the inland waters in EU (Directive 2008/105/EC) (Table 1). P. fluviatilis specimens were placed into tanks with continuously aerated dilution water. The fish were divided into 4 groups of 7 (altogether 28 fish) and placed into 4 tanks in which received one of the following treatments: 1) no parasite treatment and no exposure to metal mixture MIX (uninfected control), 2) co-infection and exposed to metal mixture MIX (infected MIX), 3) co-infection and no exposure to metal mixture MIX (infected control), 4) no parasite treatment, only exposure to metal mixture MIX (uninfected MIX). Clean water and test solutions were daily renewed, test fish (after feeding) were transferred into newly prepared solutions.

### Cell isolation and nuclear abnormalities (NAs) assay

From the caudal vein of *P. fluviatilis* specimens, peripheral blood samples were collected with a sterile syringe. A drop of blood was smeared on slides and dried. Smears were fixed with methanol (for 10 min.) and later stained with Giemsa solution (10%) in phosphate buffer (pH 6.8) for 40 min. The analysis of nuclear abnormalities (NAs) such as micronucleus (MN) (Fig.1. A), blebbed nuclei (BL) (Fig.1. B) and nuclear buds (NB) (Fig. 1. C) was performed in erythrocytes of peripheral blood. The slides were analyzed using a light microscope Olympus BX51 (Tokyo, Japan) at a magnification of 1000x. The identification of NAs was done by the criteria described by Heddle et al. (1991)[8] and Fenech et al. (2003)[9]. The frequencies of abnormalities were recorded in 4000 erythrocytes per slide using blind scoring. Per mills (‰) were counted.



Fig. 1. Nuclear abnormalities: A - micronucleus, B - blebbed nucleus, C - nuclear bud

### Statistical analysis

For normality, all data groups separately were tested using Shaphiro-Wilk test, for homogeneity of variance Levene's test was performed. To reveal differences between groups, multiple-comparison tests (one-way ANOVA, Turkey post-hoc test) were performed. The level of significance was established at p < 0.05 (RStudio 1.2.5042, © 2009-2020 RStudio, Inc.). The results were expressed as box plots where middle line marks Median (Q<sub>2</sub>), box represents the interquartile range (IQR) (data from 25<sup>th</sup> percentile (Q<sub>1</sub>) to 75<sup>th</sup> percentile (Q<sub>3</sub>)), separate dots mark potential outliers and remaining data on the strings from minimum to maximum values in the data (without extreme values).

# RESULTS

We evaluated genotoxicity levels caused by multiple stressors (exposure to metal mixture and co-infection with *Trichodina sp.* and *S. parasitica*) in *P. fluviatilis* observing nuclear abnormalities. The highest frequency of MN (Fig. 2) was observed in fish exposed to metal mixture (values varied from 0 ‰ to 0.5 ‰), but the changes were not statistically significant (p > 0.05) compared to control group. The highest and statistically significant frequencies of NB (Fig. 3) were observed in co-infected and exposed to the metal mixture fish (values varied from 0.25 ‰ to 1.75 ‰). The frequencies of BL (Fig. 4) endpoint followed the sequence uninfected MIX > infected MIX > uninfected control > infected control. Blebbed nuclei frequency observed in a group only exposed to metal mixture significantly differ from BL frequency measured in the infected control group. The most commonly observed nuclear abnormality was nuclear buds (maximum value -1.75 ‰).


Fig. 2. Micronuclei (MN, ‰) observed in different groups of *P. fluviatilis*. Group indicate different treatments. Uninfected MIX –treatment only with the metal mixture, no infection with parasites. Uninfected CTRL – no metal mixture treatment or infection with parasites. Infected MIX – both infection and metal mixture treatment. Infected CRTL – only infected with parasites. Dots indicate separate individuals. Letters denote significant differences among groups



Fig. 3. Nuclear buds (NB, ‰) observed in different groups of *P. fluviatilis*. Group indicate different treatments. Uninfected MIX –treatment only with the metal mixture, no infection with parasites. Uninfected CTRL – no metal mixture treatment or infection with parasites. Infected MIX – both infection and metal mixture treatment. Infected CRTL – only infected with parasites. Dots indicate separate individuals. Letters denote significant differences among groups



Fig. 4. Blebbed nuclei (BL, ‰) observed in different groups of *P. fluviatilis*. Group indicate different treatments. Uninfected MIX – treatment only with the metal mixture, no infection with parasites. Uninfected CTRL – no metal mixture treatment or infection with parasites. Infected MIX – both infection and metal mixture treatment. Infected CRTL – only infected with parasites. Dots indicate separate individuals. Letters denote significant differences among groups

#### DISCUSSION

The present study addresses the question of whether the combination of parasitic coinfection and metal mixture evokes a stress response in *P. fluviatilis*. With this study, we managed to evaluate occurring genotoxicity levels during simultaneous exposure to these stressors. The results show that overall genotoxicity levels were the highest in both co-infected and exposed to multicomponent metal mixture specimens groups. However, no correlation between all three studied nuclear abnormalities levels was observed. This may suggest that NAs occur independently to one another. The lowest genotoxicity levels were observed in the control group (uninfected CTRL), although some NAs were still present. Very little is known about the genotoxic response that occurs in animals under the influence of multiple stressors. Several studies [10, 11] have described the genotoxicity of mammalian parasitoses. Genotoxicity could be induced by the release of parasite products [10]. Some of the parasite-produced metabolic products are known to be highly immunogenic [12] and thus can lead to genetic instability [11]. Based on the results of this study, it can be concluded that the stressors studied may act synergistically. Unfortunately, we cannot predict which stressors cause more genotoxic damage to cells. MN and BL endpoints were more associated with the effect of the metal mixture and the formation of NB – with co-infection or multiple stressors treatments. MN are induced by clastogens or aneugens during cell division [13]. Nuclear buds and BL are biomarkers of gene amplification and elimination of amplified DNA, DNA repair complexes and possibly excess chromosomes from aneuploid cells [14, 15].

In summary, fish communities in aquatic ecosystems are affected by multiple stressors simultaneously, confirming the need for more comprehensive ecotoxicological studies to conserve and restore ecosystems under changing climatic conditions. Therefore, the effects of identified stressors need to be further investigated in order to understand whether concurrent stressors evoke additive, synergistic or even antagonistic effects at the cellular level.

# CONCLUSIONS

- Genotoxic responses in fish erythrocytes are highly influenced by the origin and type of the stressor (natural, anthropogenic or biotic, abiotic).
- Mixed infections weaken *P. fluviatilis* resistance to chemical stress.
- Heavy metals and parasitic co-infections caused a synergistic genotoxic effect (NB) in fish.

# ACKNOWLEDGEMENTS

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# THE RECONSTRUCTION POSSIBILITIES OF GROUNDWATER DATA SERIES WITH GAPS INTRODUCED AT A PILOT AREA IN BUDAPEST

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#### ABSTRACT

Groundwater always plays a significant role along riverbank area. If it is a habitat for riparian ecosystems, the goal is estimating the optimal groundwater stages for certain vegetations. Furthermore, in municipal areas, data is required to get to know the effects of human activity, such as buildings reaching the aquifer, like at the Lágymányos pilot area in Budapest, Hungary. Here the groundwater levels are highly influenced by the level of the river Danube.

Over the area a series of piezometer wells are set to observe groundwater levels, but only one is equipped with continuous recorder, the others are measured occasionally with a manual water level meter. The aim of this research is to set connection between the continuously recorded levels and the occasionally observed ones and reconstruct the time series of each observation well as accurate as possible.

After introducing the area and evaluating the most important methods of groundwater level observation, the continuous and occasionally measured time series are analysed. First connection is set between the data series of the continuously registered well and the occasional measurements for each observation wells with linear regression. This analysis showed weaker connection at the piezometers near the river than with the further ones, proving the strong influence of the river.

Applying multiple correlation made it possible to involve the effect of the river into the analysis too. It proved higher correlation factor for each well, making it possible to reconstruct their daily water levels with high reliability not only for shorter or longer gaps, but even in case of an earlier abandoned piezometer as well. The simple regression formulae for each well give better estimation of the groundwater regime of the area and help the safer design and operation of buildings and other structures situated along riverbank area.

Keywords: measurement of groundwater levels, data series with gaps, regression analysis

# **INTRODUCTION**

A significant part of Hungary's capital is on the former floodplain of the Danube. One of these places in Budapest is Lágymányos [1], which is partly formed on the filled-up riverbed. In such areas the current water level of the river has a significant effect on the groundwater.

In municipal areas, not only the natural processes, but the buildings also affect the groundwater movement, by reaching the aquifer. This Lágymányos pilot area is in the south part of Buda, between the Petőfi bridge and the Rákóczi bridge, where the area is constantly evolving with university and office buildings.

The filling of the area is a mixed material, with the main component being slag from a nearby power station [2]. This slag contains some heavy metal with a quantity that can exceed health limit. To control the wash out of this dangerous material, the environmental authority prescribed the setting and operation of several monitoring wells. So seven wells were set on the area as shown on Fig. 1. Though they are originally for water quality control, the levels were also recorded from 2004 [3]. The obligatory period of water quality observations ended after

the required ten years, but to avoid the demolition of the wells, TU Budapest took over their operation for study and education purposes. Since then only quantitative measurements are executed. The groundwater level measurements are going on for more than 15 years to this day [4].



Fig. 1. The wells in the pilot area.

Unfortunately, the well TVF was abandoned in the summer of 2016 by local authorities, so only the remaining six wells are available for further examinations in the future, but enough data were collected to include in this analysis.

The aim of this paper is to reveal the interaction between the groundwater levels of the wells and the river Danube, and with this knowledge, to reconstruct their daily data series, that are more suitable to solve several problems in the field of construction management and also when calibrating groundwater models.

# MEASUREMENTS

Determining the groundwater level usually means the measurement of the distance between a reference level – usually the top of the well casing – and the water level in the well. So, something has to be hung in the well that gives a sign when reaching the water level. A traditional way is the whistle that gives a sound (Fig. 2., left). But in a busy city traffic that weak sound is hard to recognize. Therefor we applied a groundwater meter that turns the light of a bulb on (Fig. 2. middle).



Fig. 2. Water level meter with whistle (*left*), Water level meter with light bulb (*middle*), Continuous water level recorder in well (*right*)

The formerly seven, now six groundwater wells are measured mainly once a month since 2015 to this day with a manual water level meter. These measurements have bigger, one-month long time steps, but there are several cases, when a denser data series is advantageous. Therefore in the spring of 2016 a Dataqua[5] continuous water level recorder (Figure 2, right) was installed in the GWM-31 well. This choice was based on the following considerations:

- The wells on the riverside were excluded, as the influence of the Danube would have dominated.
- The TVF well was inadequate because its existence was already questionable by then.
- ELTE-1 is behind a larger building, and GWM-21 is between several buildings.

Thus, the GWM-31, the second most distant well to the Danube was found to be the most suitable.

The continuous water level recorder stored the measured water levels every hour, but they were filtered for further evaluations for every 24 hours. Since the manual measurements were mainly performed during the day, the 12 o'clock data were retained.

The daily water levels of the Danube are taken at the Vigadó Square main gauge station at about 2,5 km upstream from the site. Water levels are available at the website of the Hungarian Hydrological Forecasting Service [6].

In the further computations to give a reliable estimation of these denser data series that are more suitable for a given problem, the manual measurements for the six (later five) wells, the recorded water levels in the GWM-31 well and the river Danube's water levels were used, uniformly in meter above sea level for better comparability.

The measurements were accomplished during low and medium water level, as since the remarkable flood of 2013, a rather low water period continued even until today.

# **RECONSTRUCTING THE DAILY DATA SERIES OF THE WELLS**

## Linear regression with the continuously registered well

First, the connection is set between the data series of the continuously registered well and the regular measurements for each observation well with linear regression, as shown in Fig. 3. The GWM-31's water levels are on the horizontal axis, the observed groundwater levels in the other five wells are on the vertical axis. The markers show the measured data, and the lines present the correlation lines.



Fig. 3. Linear regression with the well GWM-31

The correlation factors are showed in Table 1., most of them are larger than 0.8, expect at the two riverside wells, that have significantly smaller factors. This suggested that they have a stronger connection to the river Danube.

## Linear regression with the river Danube's water levels

To further investigate the relationship with the river, the connection is set between the daily water levels of the Danube and the occasional measurements for each observation well with linear regression.

The results are shown Fig. 4., where the horizontal axis is the Danube's water levels, the vertical axis still represents the wells' levels.



Fig. 4. Linear regression with the water levels of the river Danube

The correlation factors computed with this method are also showed in Table 1. The two wells nearest to the river show higher factors, but the other wells have smaller ones now than in the first case, but still higher than 0.7. This shows, that although the base flow is towards the Danube - as it was a continuous low water period, the Danube is still an important influencing factor.

Table 1. Correlation factor	ors
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	ELTE-1	ELTE-2	ELTE-3	GWM-11	GWM-21	TVF
Correlation to the well GWM-31	0,86	0,66	0,77	0,86	0,88	0,93
Correlation to river Danube	0,83	0,88	0,89	0,79	0,77	0,88
Multiple correlation	0,93	0,89	0,92	0,91	0,92	0,95

## **Multiple correlation**

To get a better estimation of the groundwater regime of the area, the connection is set between the manual observations for the wells, the recorded water levels in the GWM-31 well and the river Danube's water levels with multiple correlation [7][8]. The independent variables are the GWM-31's groundwater levels (x) and the Danube's water levels (z), and the dependent variable is the currently examined well (y). Five equation were formed this way (1 to 5):

$$y_{ELTE-1} = 0.68 * \left( \chi_{GWM-31} - \overline{\chi_{GWM-31}} \right) + 0.25 * \left( Z_{Duna(Vigad)} - \overline{Z_{Duna(Vigad)}} \right) + \overline{y_{ELTE-1}}$$
(1)

$$y_{ELTE-2} = 0.27 * (\chi_{GWM-31} - \overline{\chi_{GWM-31}}) + 0.62 * (\chi_{Duna(Vigado)} - \overline{\chi_{Duna(Vigado)}}) + y_{ELTE-2}$$
(2)

$$y_{ELTE-3} = 0.54 * (\chi_{GWM-31} - \chi_{GWM-31}) + 0.51 * (\chi_{Duna(Vigad)} - \chi_{Duna(Vigad)}) + y_{ELTE-3}$$
(3)

$$y_{GWM-21} = 0.80 * (\chi_{GWM-31} - \chi_{GWM-31}) + 0.18 * (\chi_{Duna(Vigad\delta)} - \chi_{Duna(Vigad\delta)}) + y_{GWM-21}.$$
 (5)

This way all the correlation factors are larger, about 0,9 as shown in the last row of Table 1. Table 2. shows the different root mean square errors (RMSE) [9] for the three techniques, and the multiple correlation appears to be more accurate with the smallest error. With this method, the daily data series of the wells can be reconstructed with high accuracy, when the GWM-31 and Danube's water levels are known.

<b>RMSE</b> when computed with:	ELTE-1	ELTE-2	ELTE-3	GWM-11	GWM-21
data of well GWM-31	0.16	0.43	0.33	0.15	0.11
Danube level	0.19	0.17	0.14	0.23	0.23
multiple correlation	0.06	0.18	0.08	0.09	0.07

Table 2. Root mean square errors (RMSE) for the different methods

## **Further comparisons**

In the following, the computed data series of two specific wells are compared. One of them is the ELTE-3, which is a riverside well with the highest correlation factor to the Danube, and the other one is the GWM-21, which is the most surrounded by buildings.



Fig. 5. Computed groundwater levels for the well ELTE-3 (with 3 method)

Fig. 5. shows the ELTE-3 reconstructed data series computed with the three different methods for the first half of 2016.



Fig. 6. Computed groundwater levels at the well GWM-21 (with 3 method)

Fig. 6. shows the GWM-21 reconstructed data series computed with the three different methods, for the same period, with similar notations.

In accordance with the former point, the data series computed with multiple correlation shows the highest accuracy compared to the observed water levels.

#### **RECONSTRUCTING THE DAILY DATA SERIES OF AN ABANDONED WELL**

The TVF well was abandoned before the summer of 2016. Fortunately, I was still able to collect enough data in this short period of time, to accomplish the multiple correlation. With the help of the resulted correlation equation (6), the TVF well's data series were determined for the summer of 2016.



Fig. 7. Computed and observed water levels (2016.07.20.-2017.09.06.)

In Fig. 7., the continuous lines represent the water levels of the river Danube and the well GWM-31, and the reconstructed daily data series of the six other wells. The observed groundwater levels of the six wells without continuous recorder are shown with the markers. The well TVF's last observation is indicated with a green marker, and its reconstruated daily data series (solid green line) nicely follows the characteristics of the other wells.

According to Fig. 7., the river's floodwaves cause the slightest rise in the groundwater at the TVF well, which is the farthest from the Danube. It is also true, that when the river's water level is decreasing, the TVF well shows the characteristics of the other farther located wells. It is important to note, that the river's smaller floodwave at the end of August did not cause a significant wave in these wells, just as the TVF's reconstructed data series also shows.

Fig. 7. also shows the importance of the continuous recording of the groundwater levels. Just with the regular manual observations, the effects of the smaller floodwaves (at the end of July and in the middle of August) would not be taken into account otherwise.

## **DISCUSSION AND FURTHER RESULTS**

The multiple correlation technique presented above is a suitable method to predict groundwater levels. It has several important practical advantages compared to artificial neural network techniques [10], as it is less time-consuming and labour-intensive, and can be a cost-effective tool in situations when the field data is appropriate.

As a further step to investigate the proper use and the required quantity of the measured data, the observations were extended for 2017 too. With the same method the multiple correlation equations were determined with the data from 2017 and also with all the data from the two examined years together. Table 3. contains the computed RMSE values and the correlation factors are shown in Fig. 8.

	ELTE-1	ELTE-2	ELTE-3	GWM-11	GWM-21
RMSE when computed with data from 2016	0.12	0.16	0.12	0.21	0.11
RMSE when computed with data from 2017	0.15	0.11	0.13	0.22	0.15
RMSE when computed with data from both years	0.10	0.09	0.10	0.16	0.10

Table 3. Root mean square errors (RMSE) for the different time intervals

According to that, it is clear that the data series computed with the data from one year period already show high connections with the observations. But on the other hand, the RMSE for all the wells is the lowest when the equations are determined with two years of data, so the longer the observations are performed, the approximation can be more precise and more reliable. This is also true for the highest correlation factors at almost all wells.



Fig. 8. Correlation factors

The well GWM-11 is the only one whose behaviour is significantly different, the correlation factor is the lowest, RMSE is the highest for all three time intervals. The explanation for this is that a large-scale riverside construction was in process in this year, in the neighbourhood of this particular well. This phenomenon points out that only homogeneous observed data series are adequate for this correlation analysis and similar construction works or other disturbance are able to disrupt the continuous observations. According to these, the GWM-11 characteristics should be treated with criticism.



Fig. 9. The maximum, minimum and mean values of the differences between the observed and computed groundwater levels

The comparison of the difference between the observed and computed groundwater levels is another possible option to determine the accuracy of the different data series. The maximum, minimum and mean values of these differences are shown on Fig. 9.

This also shows, that the difference is usually smaller when longer data series are used to the calculation. This also can be seen at the well GWM-11, which proves that the high RMSE and low correlation factor with the data from 2017 was not caused by fault measurements, but from the inhomogeneous data series.



Fig. 10. Computed daily data series of the well ELTE-3



Fig. 11. Computed daily data series of the well GWM-21

The next comparison option is to examine directly the daily data series for the same time period of 2017. They are shown for ELTE-3 (Fig. 10.) and GWM-21 (Fig. 11.) as previously on Fig. 5. and Fig. 6. It is clear, that considering only one year of observation is enough for the estimated daily data series, as they do not show major differences. But the previously introduced deeper investigations show that considering data from 2 years has higher correlation factors and smaller RMSE.

To summarize, the longer the data series, the more accurate the estimation is. But the homogeneity of the data series always has to be kept in mind.

# SUMMARY

The aim of this research was to analyse the connections in a group of groundwater wells, where one is equipped with continuous recorder, and to reconstruct the daily data series of the occasionally measured wells with the help of the gathered data. As the Lágymányos pilot area is located next to the Danube, the relation between the river and the groundwater was needed to be taken into account. Based on the results, the following conclusions are made:

- Groundwater level monitoring wells located in a smaller area can be treated together as a group. It is enough to continuously register the groundwater levels only in one well, which is preferably centered, not affected by other effects. Then the regular, manual measurements in the other wells are adequate, as the reconstruction of their continuous data series is possible with regression analysis. However, the impact of the area size requires further research.

- If the area is bounded by a river, the water level of the river needs to be treated as a new independent variable, so the correlation will be multivariable.

- The calculations can only be performed with a homogeneous data set, that not only means the absence of major interventions and constructions, as greater floods can also modify the relationships [11].

- In this case, a one-year long data series in the time period of low and medium water level is acceptable to set up the connections, but the longer the data series, the more accurate the estimation is. Further analysis is needed to identify the main modifying interventions, as there are models that require the use of nine-year-long data series [12].

In conclusion, the connection equations set up with multiple correlation in the above way are suitable for reconstruct groundwater data series with gaps in the covered water level range, for increasing the number of data in a time series, and for determine the groundwater levels at the place of an abandoned groundwater monitoring well. These are all problems in construction and calibration of groundwater models, as missing data in long time period can be a reason for exclusion for further using a gauging station [13], and solving them gives more opportunities to use more, denser and longer data series for future studies.

The groundwater measurements are still going on. Presently the aim is at one hand to check the required length of the time period to be taken into consideration and at the other hand to reveal connections between the parameters of equations 1 to 5 and the Danube level or other influencing factors, like the precipitation.

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# THE INFLUENCE OF VARIOUS AMENDMENTS ON CHANGES IN SOIL ORGANIC CARBON IN DIFFERENT SOIL LAYERS

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#### ABSTRACT

The use of organic amendments in agriculture is a common practice due to their potential to increase crop productivity and enhance soil health. Indeed, various amendments of different origin and composition, such as lime sludge, catch crops for green manure or winter mulch, can provide valuable nutrients to the soil as well as increase the amount of soil organic matter (SOM), thus benefiting soil improvement. Lime sludge from a sugar factory can be used to replenish soil organic matter. However, in Lithuania, the residual effect of lime sludge on soil agrochemical properties has not been studied. Biomass of catch crops grown and incorporated into the soil also increases soil organic carbon (SOC). Soil mulching has multiple benefits, as decomposing mulch adds nutrients to the soil, retains nutrients in the plant root zone, and reduces nutrient leaching.

The aim of this study was to determine the changes in SOC due to the long-term effects of different amendments: cover crops for green manure and for winter mulch, and residual effect of lime sludge. The research was carried out in 2016–2018 at the Joniskelis Experimental Station of the LRCAF on a clay loam soil in the long-term experiment, established in 2006. The following tillage systems were investigated: deep ploughing without organic amendment (DP), ploughless tillage with lime sludge incorporation (PT+LS), ploughless tillage with cover crops for green manure (PT+GM), no-till with cover crop for winter mulch (NT+WM). The field trial was laid out in a randomized single row design with four replicates. Each tilled sub-plot size was  $16 \times 5 = 80$  m<sup>2</sup>, of which  $13 \times 2.3 = 29.9$  m<sup>2</sup> was harvested. The experiment was conducted in the crop rotation: field pea (*Pisum sativum* L. (Partim)  $\rightarrow$ winter wheat (*Triticum aestivum* L.)  $\rightarrow$  spring oilseed rape (*Brasica napus* L.)  $\rightarrow$  spring barley (Hordeum vulgare L.). Cover crops were grown as follows: before field pea - a mixture of white mustard (Sinapis alba L.) and oilseed radish (Raphanus sativus L.), before spring oilseed rape – a mixture of field pea, common vetch (Vicia sativa L.) and blue lupine (Lupinus angustifolius L.), before spring barley – oat (Avena sativa L.). The straw of the pre-crop was chopped during harvesting and incorporated into the soil at 6-8 cm depth; post-harvest cover crops were sown after stubble cultivation. Lime sludge (7.0 t ha-1) was incorporated three times for spring crops during the first stage of the experiment (2007-2010) and once for spring barley during the second stage of the experiment (2011-2014) to improve soil physical properties and structure, but the soil acidity in the plough layer reached the level of neutral and slightly alkaline soils (pH = 7.2) and only the residual effect of lime sludge was investigated in this experiment. Cover crop for winter mulch was left intact in the autumn, and its frostkilled residues covered the soil. All rotational crops were fertilized with  $N_{30}P_{90}K_{60}$  before sowing. The changes in SOC content were measured in the soil samples collected from 0-10, 10-20 and 20-30 cm layers. Significant differences among experimental treatment means were assessed by Fisher's LSD test at the 0.05 probability level.

Our experiment showed, that lime sludge, green manure and mulch did not increase humus content significantly, however significant differences were found in soil layers. The increased humus content was established in all treatments of reduced tillage with soil improvement practices compared to DP (control) in 0–10 cm soil layer. The application of PT+LS, PT+GM and NT+WM increased the humus content by 15%, 14% and by 10% compared to the control DP. However, significantly higher humus content was determined under ploughless tillage with green manure (PT+GM) treatments.

The use of amendments significantly increased the SOC content only in the upper 0-10 cm arable layer: the application of PT+LS and PT+GM increased the SOC content by 12%, and NT+WM – by 9% compared to the control DP. A downward trend in SOC was observed in the 10–20 and 20–30 cm arable layers, but no significant differences were found.

Application of DP resulted in significantly higher amount of SOC content in the upper (0-10 cm) topsoil layer. Due to PT+LS, PT+GM and NT + WM, the SOC content in the 10–20 cm layer was not significantly affected.

The humification degree (HD) values at 0-30 cm soil layer ranged from 32.24% in 20-30 cm layer to 38.24% in 20-30 cm layer. HD increased significantly by 7% in the 10-20 cm soil layer after the application of PT + LS compared to DP.

Keywords: soil organic carbon, lime sludge, catch crops, green manure, winter mulch

# PIG MANURE BIOCHAR WITH INORGANIC NITROGEN FERTILIZER REDUCES SOIL CO<sub>2</sub>, N<sub>2</sub>O, AND CH<sub>4</sub> EMISSIONS

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#### ABSTRACT

Nitrogen fertilization significantly increases greenhouse gases (GHGs) emission, when applied from inorganic or organic sources. Minimizing GHGs from agroecosystems without compromising crop yield for stabilization of green production systems remains a challenge. Being an integral component of crop technology, the nitrogen (N) application deems to be indispensable. Thus, to reduce the application of N fertilizer and keep in view the minimization of GHGs emission, without compromising soil fertility and crop production, field experiments were performed with treatments included Pig digestate biochar (550 °C) e.g. (control), fertiliser 180 kg ha<sup>-1</sup> (N2), fertiliser 120 kg ha<sup>-1</sup> (N1), Pig digestate derived biochar 25 ton ha<sup>-1</sup> (B), N2+B, and N during 2020. Results showed that the cumulative CO<sub>2</sub>, N<sub>2</sub>O and CH<sub>4</sub> emission from N2B treatments significantly decreased by 10%, 1.6% and 4.6%, respectively, compared with that of B treatment without any inorganic fertilizer application. Similarly, the N2B treatment lowered global warming potential (GWP) caused by CO<sub>2</sub>, N<sub>2</sub>O and CH<sub>4</sub> emission by 16.78%, 31.39% and 25.54% respectively compared with that of B treatment. Likewise, the average soil moisture content significantly increased by 5% and 8.6% for N2B, and N1B treatments at 0-10 cm soil depth, respectively, compared to control treatment and had lowered the soil temperature by 0.2 and 0.1 °C, respectively. Therefore, biochar combined with 70% recommended doses of N (120 kg ha<sup>-1</sup>) fertilizer treatment (N2B) from commercial source were considered as a viable production technology to mitigate GHGs emission and GWP.

Keywords: Biochar; Greenhouse gasses emission; Global warming potential, Soil moisture; Soil temperature

# **INTRODUCTION**

Water and food security are the biggest obstacles under climate change as both are highly susceptible to continuously changing climatic patterns. It is predicted that by the end of the 21st century the average global temperature may rise-up by 1.4-5.8 °C and there would be significant decline in fresh water reserves and crop yield [1]. Growing at slower pace, world population is expected to reach 9.7 billion by 2050 which will cause serious challenges to agrofarming for ensuring food security with minimum impacts on water, soil, and climat [2]. The demand for organic products has been growing globally for about a decade. The representative survey conducted by the research company Spinter tyrimai showed that 76% of Lithuanian population associate the consumption of organic products with health and quality of life. Similar, 74% of people in Lithuania would support the idea of banning the use of any chemical fertilizers in agriculture without effecting crop yield [3]. Farming practices, such as inorganic fertilizers and soil tillage operations have imparted to boost greenhouse gases (GHGs) emission, particularly CO<sub>2</sub>, N<sub>2</sub>O and CH<sub>4</sub> [4], [5] On other side, fertilization is needed for proper plant growth and development [6]. The increasing use of N fertilizer in crop production has been identified as a main contributor for rising atmospheric  $N_2O$  concentration [7]–[9] which is directly affected by biochar amendment. Biochar is a porus structure byproduct of forest or agriculture residues etc, prepared through pyrolysis at temprature ranging from 200 to 900 °C [10]. Biochar application improves nutrient and water holding capicity and regulates the soil temperature, thus improving the soil moisture and temperature seems to offset the GHGs emission [6], [11]. The addition of biochar material enhanced the soil carbon, and hence resulted in C sequestration [12]. In addition to improving Soil organic carbon (SOC) stock, moisture conservation, and temperature, the biochar amendment also improves the production system and minimizes the excessive use of synthetic fertilizers [13]. Such practices can improve the environmental quality and human health by reducing synthetic fertilizers [14]. The withdrawal of subsides on chemical fertilizers by the Chinese government to avoid the overuse of chemical fertilizers for reducing the environmental pollution necessitates to search for the usage of alternative N fertilization approaches [15], [16]. Biochar addition also increases functionality related to carbon and N metabolism via increasing the microbes (Pokharel, Ma, & Chang, 2020) and thus greatly contributes to CO<sub>2</sub> and N<sub>2</sub>O emissions [17]. However, in several cases co-use of biocahr and inorganic N fertilizer reduces the N2O emission without compromising crop yield [18]. Co-application of biochar and balanced fertilizer increased maize yield, nutrients availability and decreased N<sub>2</sub>O emission [15]. Spring barley is on the major crop grown in Lithuania however during spring barley cropping system, the information on the addition of biochar with or without inorganic fertilizer on the following barley crop performance and its impact on GHG emission has not yet been documented. Therefore, it was hypothesized that the addition of pigmanure biochar (550c) with less chemical fertilizer usage will reduce the GHG emission without compromising the yield. Thus, this experiment mitigating the environment without compromising crop yield coupled with reduced synthetic fertilizers were carried out in the agriculture field of Lithuanian Research Center for Agriculture and Forestry. The main objectives of this study were to reduce the overuse of inorganic fertilizer, especially N fertilizer without compromising the crop yield coupled with improving the environmental quality by reducing the GHG emissions, and to assess the use of pigmanure biochar as an alternative source of fertilizer for barley production in Lithuania.

# **MATERIAL METHOD**

# **Experimental Site**

The experimental study was carried out in the fields of Lithuania Research Centre for Agriculture and Forestry (55°40' N, 23°87' E) during the 2020 growing seasons. The soil of the experimental fields was Endocalcari-Epihypogleyic Cambisol, characterised by a homogeneous texture and the chemical composition at a depth of 0-20 cm. The experiment was set with spring barley (Hordeum vulgare) in 2020 respectively. Annual precipitation, air temperature and humidity data was obtained from metrological department of Dotnuvos region, are presented in Fig 1. There was a bit drought-ness recorded in the year 2020 due to less precipitation at the end of 2019 and start of 2020.



Figure 1. Mean monthly precipitation (mm), air temperature (°C) and humidity (%)

## **Experimental Design**

The field experiment was established in three replicates in a complete randomised design with 6 treatments. Each treatment plot was 1.5m<sup>2</sup>. The experimental treatments were as follows: unfertilised (control), fertiliser 180 kg ha-1 (N2), fertiliser 120 kg ha-1 (N1), Pig digestate derived biochar 25 ton ha<sup>-1</sup> (B), N2+B, and N. Psyco-chemical properties of soil and biochar are given in table 1.

### Gas sampling and flux calculation

The fluxes were measured by the static chamber-gas and measured using gas chromatography technique [19] with slight modifications. The chamber base box (frame) has a U-shaped groove (50 mm wide and 50 mm deep) at the top edge to hold a removable chamber box. Gas samples were taken using a well-sealed 20cc syringe. The frames made from stainless steel were permanently installed in the ground. The area enclosed by the frame was 0.168 m<sup>2</sup>. The fluxes of CO<sub>2</sub>, N<sub>2</sub>O and CH<sub>4</sub>, were measured at two weeks interval from the start of the cultivating season (four weeks before the start of digestate application) to the next two months after harvest. The samples were analysed with a gas chromatograph (HP 6890 Series, GC System, Hwelett, Packard, USA) equipped with flame ionisation (FID) and electron capture detectors (ECD) and nickel catalyst for converting CO<sub>2</sub> to CH<sub>4</sub>. The temperatures of the GC oven, FID and ECD were 70 °C, 300 °C and 350 °C respectively. The gas chromatography procedures were as described by [19]. The cumulative flux rates of CO<sub>2</sub>, N<sub>2</sub>O and CH<sub>4</sub> over the growing season were calculated by linear interpolation between the daily fluxes [20]. The flux rate of each GHG was calculated based on the rate of change in GHG concentration within

the chamber, estimated as the slope of the linear regression between the GHG concentration and gas sampling time.

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Treatments	Soil	Biochar
pH	6.9	9.1
Total P mg kg <sup>-1</sup>	154	21.98
Total N mg kg <sup>-1</sup>	0.14	19.18
Total K mg kg <sup>-1</sup>	215	89.17
Total Ca mg kg <sup>-1</sup>	1.10	41.38
Total Mg mg kg <sup>-1</sup>	0.01	10.50
Organic C %	1.00	62.33
NH <sub>4</sub> -N mg kg <sup>-1</sup>	1.21	-
Mineral N mg kg <sup>-1</sup>	11.21	-
N <sub>2</sub> O+NO <sub>2</sub> mg kg <sup>-1</sup>	11.21	-

Table 1. Physco-chemical properties of soil and biochar

# **Statistical Analysis**

A statistics 8.1 statistical package program was used to perform statistical analysis of the data. One-way analysis of variance (ANOVA) were used to assess the statistical significance of the biochar treatment. Variability in the data was expressed as the standard error, and the level of significance was set at P value <0.05.

# RESULTS

# Impact of biochar on soil moisture content, soil temperature at different growth stages

The interactive effect of biochar on soil moisture and temperature was analysed at different growth stage of crop. During jointing stage there was huge moisture recorded 20-30% compare to tillering and maturity stages 9-18% and 12-17% respectively. Since the weather condition fluctuated during the year 2020 and biochar showed its impact Fig. 2. Similarly there was big fluctuation recorded for temperature as well. During jointing stage, soil temperature was recorded higher 30 °C compare to the rest of growing stages Fig. 2. There was strong correlation reported between GHGs and soil moisture and soil temperature Fig. 4.



Figure 2. Changes in soil moisture content (%) and soil temperature (°C) in different growth stages of barley crop. Note Growth stages: S= Seedling, T= Tillering, J=Jointing, F= Flowering Stage, GF= Grain Filling, M=Maturity

## Cumulative emission of GHGs and Global warming potential

Cumulative emission of CO2, N2O and CH4 was found significantly higher 17.98%, 3.4% and 4.2% respectively in N1B treatment compare to N2B treatment. Treatment N1B was also found significantly higher 20.14%, 2.1% and 2.37% respectively compare to N1 treatment (Table 2). Global warming potential (GWP) CO2 was recorded significantly higher 2.91% 4.37% respectively in control and N1 treatments compare to B treatment. Whereas GWP N20 was found significantly higher 32.55% in N2 treatment compare to N2B treatment. GWP CH4 for treatment B was found significantly higher 25.54% compare to N2B treatment (Table 2).

Table 2. Cumulative CO<sub>2</sub>–C (mg ha<sup>-1</sup> day<sup>-1</sup>), N<sub>2</sub>O–N (μm m<sup>-2</sup> min<sup>-1</sup>) CH<sub>4</sub> (μm m<sup>-2</sup> min<sup>-1</sup>) emission and Global warming potential (GWP) under different treatments

Treatments	Cumulative CO <sub>2</sub>	Cumulative N <sub>2</sub> O	Cumulative CH <sub>4</sub>	$\frac{\text{GWP CO}_2}{(\text{mg ha}^{-1} \text{ day}^{-1})}$	$\frac{GWP N_2O}{(mg ha^{-1} day^{-1})}$	GWP CH <sub>4</sub> (µm m <sup>-2</sup> min <sup>-1</sup> )
Control	$13.3 \pm 0.011a$	$272.5 \pm 0.056b$	2132.8 ± 0.032ab	13.3a	2.92ab	1.42a
N2	$12.5 \pm 0.012ab$	$379.0 \pm 0.019a$	$2108.9 \pm 0.063c$	12.5ab	2.98a	1.40a
N1	$11.1 \pm 0.015b$	$375.5\pm0.021b$	$2096.5 \pm 0.068c$	13.1a	2.92ab	1.41a
В	$13.7\pm0.018ab$	$371.1\pm0.054b$	$2142.4 \pm 0.015a$	13.7b	2.93ab	1.37b
N2B	$11.4 \pm 0.013b$	$365.4 \pm 0.016c$	$2055.2 \pm 0.042 bc$	11.4ab	2.01c	1.02c
N1B	$13.9 \pm 0.012a$	$378.2 \pm 0.014a$	$2147.6 \pm 0.016a$	12.4b	2.90b	1.41a

## Impact of biochar on GHGs emission

Greenhouse gasses emission (CO<sub>2</sub>, N<sub>2</sub>O and CH<sub>4</sub>) emission at different growth stages of growing season. CO<sub>2</sub> emission flux was significantly lower jointing stages in all treatments except for the control treatment 1.12 mg ha<sup>-1</sup>. N<sub>2</sub>O emission was found lower 1.2 to 1.7 micro mole m<sup>2</sup> min<sup>-1</sup> at flowering in all treatments and maturity stages in N1 and control treatments 1.5-1.6 micro mole m<sup>2</sup> min<sup>-1</sup> respectively. CH<sub>4</sub> emission was found lower during flowering stage ranging 10.6-11.1 micro mole m<sup>2</sup> min<sup>-1</sup> in all treatments compare to other stages Fig. 3.



Figure 3. CO<sub>2</sub>, N<sub>2</sub>O and CH<sub>4</sub> emission at different growth stages of barley crop. Note Growth stages: S= Seedling, T= Tillering, J=Jointing, F= Flowering Stage, GF= Grain Filling, M=Maturity

Positive correlation was recorded between GHGs (CO<sub>2</sub>, N<sub>2</sub>O and CH<sub>4</sub>) emission and soil moisture and temperature Fig. 4. This corelation indicated that there is highly dependency among GHGs emissions and soil temperature and soil moisture.







Figure. 4. Linear relationship of soil CO<sub>2</sub>, N<sub>2</sub>O and CH<sub>4</sub> emission with soil moisture and soil temperature throughout the barley growing season

# DISCUSSION

# Global warming potential (GWP)

The net GWP was significantly higher in the plots treated with biochar and N fertilizer. Our results showed that application of recommended doses of N fertilizer (180 kg N ha<sup>-1</sup>) significantly increase GWP. The increase in GWP might be the use of inorganic fertilizer. The increase in GWP with the addition of inorganic fertilizer compared with that of oragnc amendment was in line with Pathak [21]. Further, continuous production of crop under inorganic fertilizer will produce more net GWP [22]. Likewise, the increase of 28% in GWP was reported from the application of inorganic fertilizer under rice–wheat cropping system [23].

## Soil GHGs emissions

The emissions of  $CO_2$  N<sub>2</sub>O and CH<sub>4</sub> resulted in decomposition of organic matter [24]. biochar enhanced soil fertility upon decomposition, and thus had more environmental benefits

than other chemical amendments [25]. Biochar is an external carbon source and helps in the increase of SOC accumulation [26], which cause the greater average annual CO<sub>2</sub> emission in N1B treatment than N2B, even at low soil temperature. This finding indicated that soil C had a greater potential in variability of soil CO<sub>2</sub> emission [27] and hence increased the soil fertility. Higher soil microbial activity indicated that more emission of soil CO<sub>2</sub> is regulated by soil moisture and temperature [28]. During the season, nitrogen treatments significantly affected the seasonal variations in soil CO<sub>2</sub>, N<sub>2</sub>O and CH<sub>4</sub> for crop. Likewise, during the research phases, soil moisture and temperature temporal variations were an evidence for biochar treatments. However, inconsistent results from agricultural fields showed that biochar decomposition increased soil CO<sub>2</sub>, N<sub>2</sub>O and CH<sub>4</sub> emission and soil C and N availability.

The excessive use of N fertilizer increased GHGs emission and showed adverse effects on the environment [29]. The current results revealed that the increase of biochar in combination with N fertilizer significantly increased soil N<sub>2</sub>O emission throughout winter growing seasons . Amendment fertilizers in soil normally increased N<sub>2</sub>O emissions based on emission factors of N used [30], [31]. The emission factor from organic fertilizer is difficult to be predicted due to the diversified chemical structure [30]. It is already documented that N fertilization increased the N<sub>2</sub>O flux by 71–123% along with biochar or organic treatments [32] and had shown positive interaction in all biochar treatments except onions and olea as compared to unfertilized regimes. However, N<sub>2</sub>O emission could be decreased by managing of N fertilizer according to crop needs [33].

# CONCLUSION

The GHG emission was greater during the jointing stage of barley crop with  $160 \text{ kg N ha}^{-1}$  along with 25 ton ha<sup>-1</sup> of biochar. However, reducing the N fertilizer by 20% (120 kg N ha<sup>-1</sup>) had reduced the GHG emission, coupled with improved soil moisture conservation and regulating the soil temperature without compromising the crop yield. Therefore, the re-usage of biochar with 70% of recommended dose of N fertilize is suggested a feasible approach to protect the environment by reducing soil CO<sub>2</sub>, N<sub>2</sub>O and CH<sub>4</sub> emission, and thus can be considered as alternative source of fertilizer in the cereal producing belt in Europe.

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# REVEALING THE DEPENDENCES OF THE COMPOSITION OF SYNTHETIC OILS ON THE DIFFERENT AQUATHERMOLYSIS DURATION TIMES USING THE GC-MS

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## ABSTRACT

In this study the changes of qualitative and quantitative composition of 16 priority PAHs in two series of synthetic oils obtained by aquathermolysis were investigated by gas chromatography-mass spectrometry. The total time of aquathermolysis was 10 and 12.5 days. Liquid components of the pyrolyzate were collected every 12 hours. It was shown that the amount of 16 priority polycyclic aromatic hydrocarbons (PAHs) decreases during aquathermolysis, but this dependence is not linear (it has local minima and maxima). During the process of aquathermolysis the decrease of PAHs content with 5-6 rings is observed. The bulk of the samples is occupied by medium molecular weight PAHs (with 3-4 aromatic rings). The study allows us to model a process of aromatic components generation.

Keywords: synthetic oil, aquathermolysis, polycyclic aromatic hydrocarbons, GC-MS

## INTRODUCTION

The global demand for energy today is growing while a decline in traditional oil production is observed. This has made the production and modernization of heavy and extraheavy crude oil crucial for the future of the global energy market. However, the special properties of heavy oil, such as high viscosity, high specific gravity, high percentage of asphaltenes, heteroatomic compounds, and metal-containing compounds, cause serious problems during extraction and purification processes [1]. As a result, traditional technologies are not suitable as the main method of processing such raw materials.

Synthetic oil is the products, which are derived from rocks enriched with organic matter called kerogen. The prospects for the formation of hydrocarbons from kerogen in the main high-carbon formations of Russia (the Bazhenov formation) were shown [2]. The authors show that under the influence of temperature, it is possible to partially realize the generation potential of kerogen and to obtain hydrocarbon systems of different composition.

Modelling of the process of generating petroleum products is now very common. For this purpose, aquathermolysis (thermolysis in the presence of water) is often used [3]. At the moment, in the works devoted to the study of the composition of thermolysis products, the main attention is paid to the study of the composition of the final product (hydrocarbon raw materials) under the proposed conditions, herewith the changes in its compositions over time are not investigated [4,5]. The advantages of the latter are a possibility to identify markers at various

stages of oil formation that are resistant to thermal influences and also a perspective to optimize the conditions for obtaining the final product with the most necessary consumer properties.

Polycyclic aromatic hydrocarbons (PAHs) are organic compounds, which contains two or more condensed benzene rings in the chemical structure [6]. For several decades, they have been interesting to scientists, as they have a high carcinogenic and mutagenic activity, which means that they are extremely harmful for humans.

Aromatic hydrocarbons can provide information about both the origin of the deposited organic matter and the geochemical transformations during thermal maturity [7]. It is extremely important to identify the source of PAH emissions in order to minimize pollution in the future. A large amount of PAHs enter the environment from petrogenic sources [8], so it is extremely important to study the process of their formation and distribution.

Traditionally, the content of 16 PAHs is controlled in the world [9, 10]. They are also a priority and have been controlled for a long time in many countries. All of the above was the reason for the allocation of compounds of this class to the category of priority pollutants, 16 of them are investigated in this paper.

The goal of this study is the investigation of the qualitative and quantitative composition changes of the 16 most important PAHs in synthetic oils, obtained from kerogen enriched rock, at different aquathermolysis duration times.

## **METHODS**

### **Sample collection**

The samples were provided by the Geological Faculty of the Lomonosov Moscow State University. We used 2 sets of synthetic oil samples with identification numbers 1 and 2, obtained from the rocks of the Bazhenov formation by aquathermolysis at a temperature of  $300 \,^{\circ}C$  (as was used in previous work [11]), the pressure of water vapor was 100 atm. The liquid components of the pyrolyzate were collected every 0.5 days. The samples showed different results during aquathermolysis, so our colleagues-geochemists recommended us to study the composition of sample 1 in the period from 0.5 to 12.5 days, and sample 2 - from 0.5 to 10 days. Thus, there were 2 sets of samples with a total number of 45 pieces.

### **Extraction of PAHs and analysis**

The samples were prepared according to the *SARA*-analysis (separation of samples into Saturated, Aromatic, Resins, Asphaltenes fractions). Initially, a 40-50-fold excess of *n*-hexane was added to the sample to precipitate from asphaltenes, which were not needed for further analysis. The solution was left in a dark place for a day, after which it was filtered in pre-weighed and signed glasses. The resulting solution, which contained maltenes, was dried, dissolved in 1 ml of n-hexane, and transferred to a glass chromatographic column with argent silica gel for separation into saturated and aromatic fractions. The saturated fraction was not used in further studies. The aromatic fraction was washed off in 3 portions of 1 ml of toluene.

The PAH fraction was analysed by gas chromatography (GC) coupled with mass spectrometry (MS) (Agilent 6890 GC-5977A MSD) with column HP-5MS (30 m × 0.25 mm × 0.25  $\mu$ m). Temperature conditions: initial column temperature of 60°C isotherm for 3 min, then increased the temperature from 60 °C to 180 °C at a speed of 15 ° /min from 180 °C to 300 °C at a rate of 4 C°/min, isotherm at 300 °C for 6 min. The total analysis time is 47 minutes.

We used helium as carrier gas; flow rate of carrier gas through the column -1 ml/min volume of injected sample  $-1 \mu m$ . Evaporator temperature was 290°C, the temperature of the interface -300°C. The MS data were acquired in selected ion monitoring (SIM) mode [12]. The relative abundance of compounds was determined from peak areas (using selected mass

chromatograms for the integration of the compounds). The temperature of the ion source was 230 °C, and the energy of ionizing electrons was 70 eV.

# **RESULTS AND DISCUSSION**

Total concentrations of 16 priority-controlled PAHs was counted for two sets of samples for every 12 hours. The PAH concentration decreased over the time of aquathermolysis, but this dependence cannot be called linear for any of the samples. It has local maxima and minima,





as can be seen in Fig. 1. But also we could make a conclusion, that concentration close to zero at the end of the experiment. As you can see in Fig. 1, at the beginning of aquathermolysis, the concentration of PAHs was units of grams, at the end – tenths of milligrams.

Local and global maximum a and minimum, which are shown in Fig. 1, are not the same for samples. Each set of samples has 2 local maximum: sample 1 has in 2.5 and 6.5 days, sample 2 - in 1.5 and 5.0 days. Also each set has 1 global maximum: sample 1 - 4.5 days, sample 2 -

2.5 days. It means, that PAHs quantity is increased in the first couple of days of aquathermolysis. The maximum consentration of PAHs during aquatermolysis is  $1543\pm20$ mg/kg (t = 4.5 days) in sample 1 and  $61122\pm600$  mg/kg (t = 2.5 days) in sample 2. The minimum concentration of PAHs during aquatermolysis was reached in 10.5 days for sample 1 (1.55\pm0,1 mg/kg) and in 8.5 days for sample 2 (2.44\pm0.1 mg/kg).

The content of all 16 priority PAHs in each sample was calculated for the entire time of aquathermolysis. It was found that both series of samples contain in large quantities PAHs with 4 rings, which increases after a while. Also the content of PAHs with 3 rings is decreased during the research. The content of PAHs with 5 rings is usually in a small content of about 5-15%.



Fig. 2. PAHs distribution by number of rings in samples 1 and 2 during quathermolysis

And the content of PAHs with 2 and 6 rings is minimal in comparison with other PAHs. These patterns can be observed for both series of samples in Fig. 2. Fig. 2 shows that sample 1 contains much more PAHs with 3 rings than sample 2, which is dominated almost all the time by PAHs with 4 rings.

Since PAHs with 4 rings make up most of the samples, it was decided to look at the composition of the mixture in this group of compounds. The group of priority PAHs with 4 rings studied by us includes: fluoranthene, pyrene, benz(a)anthracene and chrysene. In Fig. 3 it can be seen that the distribution of PAHs with 4 rings in samples 1 and 2 is different. In the first days of aquathermolysis, all 4 compounds are present in both samples, some in a larger amount, others in a smaller amount. However, since the beginning of a significant decrease in the total concentration of PAHs (Fig.1), the distribution of PAHs with 4 rings in the samples changes greatly. In the sample 2 after day 4, there is practically no fluoranthene; from day 4 to day 6.5, chrysene is more than 85% among PAHs with 4 rings; after day 7, the amount of chrysene is from 40 to 75%, the amount of benz(a)anthracene remains almost at the same level - 15%, and a significant amount of pyrene also reappears. In the sample 1, a completely different relationship can be observed after 5 days of aquathermolysis. The amount of pyrene is no more



Fig. 3. The distribution of PAHs with 4 rings in samples 1 and 2 during aquathermolysis than 5% until the end of the experiment; the amount of benz(a)anthracene is also small; and most of the PAHs with 4 rings are chrysene and fluoranthene. From the 5th to the 12th day, the amount of chrysene gradually decreased (from 50% to 20%), and the amount of fluoranthene on the contrary increased (from 40% to 80%).

# CONCLUSION

Thus, on the example of 2 sets of synthetic oils samples, obtained from the Bazhenov formation, the changes in the content and distribution of PAHs is shown using the GC-MS

method. For sample 1, the generation of the main PAH components ends and starts deacrease on the 4.5 day, for sample 2 - on the 2.5 day. The maximum consentration of PAHs during aquatermolysis is  $1543\pm20$ mg/kg (t = 4.5 days) in sample 1 and  $61122\pm600$  mg/kg (t = 2.5 days) in sample 2. The minimum concentration of PAHs during aquatermolysis was reached in 10.5 days for sample 1 (1.55±0,1 mg/kg) and in 8.5 days for sample 2 (2.44±0.1 mg/kg). It is noteworthy that both samples were taken from the same well, however, when studying the PAH distribution, differences were found in them. Therefore, PAHs can be considered as markers of the generation of aromatic oil compounds in laboratory modelling.

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# INFLUENCE OF DIGESTATE FERTILIZATION ON SOIL MICROBIAL ACTIVITY AND GREENHOUSE GAS EMISSIONS

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#### EXTENDED ABSTRACT

#### **OVERVIEW**

Agricultural wastes contribute significantly to global climate change through greenhouse gas emissions if not adequately recycled and sustainably managed. One recurring agricultural waste that have consistently served as feedstock for biogas systems is livestock waste. Livestock wastes are generally lower-energy feedstocks considering the pre-digestion process undergone in the digestive tracts of the animals. They are normally characterised by neutral pH, with abundant variety of microbes present, making it a choice for anaerobic digestion. The digestates which is one of the resulting products from anaerobic digestion are an excellent source of organic matter when applied to the soil. The direct application of digestate to soil is considered an inexpensive means of disposal and nutrient recovery for agricultural systems [1]. Digestate positively affects primarily biological soil properties [2] and topsoil physiological properties [3] and helps in providing the needed nitrogen, carbon source and nutrients needed for both plants to grow. The digestates have helped to tackle the challenges of reduced organic matter which have stemmed from modern agricultural technologies and over-cultivation. Aside helping to solve this problem, digestates have effectively competed with chemical fertilizers in not only mitigating greenhouse gas emissions, but it also provides nutrients, nitrogen and carbon in a form which is readily absorbed by the soil. This contributes to improving soil quality by the increasing the activities of soil microbes, thus enhancing mineralization and recycling of soil nutrients and aids in plant growth and productivity; something which is ever more important as food security is poised to become a major global issue. The soil microbes partake in the mineralization of the available nutrients present in the soil and contributes to ecosystem health in a variety of ways, including biogeochemical cycling, bioremediation, plant growth, and primary productivity [4]. Aside contributing to soil health ecosystem, their role in the sequestration of carbon and mitigating greenhouse gas emissions has received global attention in the midst of climate change. In view of the need to better understand more of the roles digestate application play in the interconnected roles in soil microbial metabolism and GHG mitigation mechanism

#### **METHODS**

#### **Experimental Site**

The experimental study was carried out in the fields of Lithuania Research Centre for Agriculture and Forestry ( $55^{\circ}40'$  N,  $23^{\circ}87'$  E) during the 2019 growing season. The field experiment was established in three replicates in a complete randomised design with 5 treatments. Each treatment plot was  $30m^2$  (3mx10m). The experimental treatments were as follows: unfertilised (control), fertilised with the synthetic nitrogen fertilizer, pig manure digestate, chicken manure digestate and cow manure digestate. The 170 kg N ha<sup>-1</sup> presented in digestates were split fertilised at an application rate of 90 and 80 kg N ha<sup>-1</sup>. All the digestate were in liquid forms. The digestates were obtained from industrial sources at three locations in Lithuania with the treatments used serving as their primary feedstocks. The digestates were spread on the soil surface without injection on the treatment plots. The experiment was set with Triticale (*Triticosecale*) in 2019.

#### Soil microbial activity

Soil dehydrogenase enzyme activity and Soil Microbial Biomass C

Dehydrogenase activity was determined according to the slightly modified method described by [5] while soil microbial biomass-carbon, was determined by using the fumigation-extraction method [6]. The organic carbon content in the extracts was measured using the dichromate digestion method.

#### Gas sampling and flux calculation

The fluxes were measured by the static chamber-gas and measured using gas chromatography technique[7] with slight modifications to determine CO<sub>2</sub>, N<sub>2</sub>O and CH<sub>4</sub> emissions. The chamber base box (frame) has a U-shaped groove (50 mm wide and 50 mm deep) at the top edge to hold a removable chamber box. The frames made from stainless steel were permanently installed in the ground, 20 cm deep into the soil. The area enclosed by the frame was 0.168 m<sup>2</sup>. For each flux measurement, the chamber was closed for 3 minutes, and the gas samples were taken in 20 ml by volume using a well-sealed 20 cc syringe. The gas samples were taken in the morning between the same time interval to improve the consistency of gaseous flux estimations.

#### **RESULTS AND DISCUSSION**

The dehydrogenase activity and soil microbial biomass-carbon could be used to predict significantly the soil microbial activity as they are easily influenced by changes in soil environmental practices and environmental practices which makes it an indicator of soil quality changes [8]. The first digestate application rate of 90 kg N ha<sup>-1</sup> resulted into higher mineralization rate and release of CO<sub>2</sub> which indicated the utilization of the N sources and available nutrient. This is also consistent with conditions in a nitrogen limited environment as the digestates and the synthetic nitrogen provided the needed mineral nitrogen necessary for microbial growth. This is in contrast to the lack of increased microbial activity in the control where inadequate carbon and nitrogen sources had a negative influence on the their growth. However, SMB-C continued to increase in the pig digestate and cow digestate until after the second fertilizer application rate of 80 kg N ha<sup>-1</sup> followed by a reduction in biomass to the same level as the control after harvest which is synonymous with the depletion of available nutrients necessary for microbial growth and activities. Control was significantly different from pig and chicken digestate after first fertilization application rate at p < 0.01. After harvest, SMB-C in control was significantly different from all other treatments at p < 0.01. Dehydrogenase activity (DHA) helps to access the enzymatic activity in the soil and serves as an indicator of microbiological redox systems and is closely correlated with aerobic activity in the soil [9]. Soil dehydrogenase activity increased slightly after the first fertilization influenced by the addition of N. Although lower DHA values was subsequently observed in all the treatments after the second fertilization with no significant differences between the treatments at the different stages of the fertilization. It was deduced that the TTC method used to measure the DHA was not suited to capture the intensive microbial activity as the level reached is indicative as probably representative of the equilibrium redox state reached after the first application rate.

For GHG emission, peaks were observed in  $N_2O$  and  $CO_2$  after the first application of fertilizers with the emissions flattening out over the cultivating season while  $CH_4$  emission was negligible with no apparent patterns observed. The treatments had no significant effect on the  $CO_2$  emission rate. The easily decomposable organic material in the digestate served as C substrate for soil microorganisms increasing the  $CO_2$  production during soil respiration. Previous results show that an enrichment in soil organic matter content positively affects  $CO_2$  emissions as emissions are related to soil respiration [10], [11] which supports the results in this study. Further study on the meteorological conditions indicated that  $CO_2$  emissions are very much influenced by soil humidity. As the precipitation was relatively low in 2019 it could be expected that results of  $CO_2$  emissions would be different in different weather conditions.

#### CONCLUSIONS

In the study, we analysed the influence of different organic digestates and their influence on the soil microbial activities as well as their involvement in GHG transformations in an agricultural soil. The study showed a similar positive traits with respect to soil microbial activities, an indicator for good soil health practices. The individual and cumulative emissions of CO2, CH4 and N2O from the digestates were lower with meteorological conditions impacting on the emissions. However, as this is a short term-study, efforts are being made to understand the underlying mechanisms of how organic fertilizers influence and possibly decrease GHG emission from agricultural soils in the long- term.
Keywords: Carbon dioxide; Nitrous oxide, Manure digestate; Soil microbial biomass

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# 5-YEARS TRENDS OF AEROSOL MAIN CHEMICAL COMPONENTS IN RŪGŠTELIŠKIS (LITHUANIA) RURAL ENVIRONMENT

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### ABSTRACT

Aerosol particles have a great influence on the atmosphere based on their chemical composition and cause environmental changes. Therefore, it is important to deepen the knowledge of aerosols chemical composition and pathways of formation.

Aerosol main chemical components were investigated in Rūgšteliškis (Lithuania) rural environment by using Aerosol Chemical Speciation Monitor (ACSM). The measurements were carried out in three seasons (Spring, Summer & Autumn) of 5 years (2013, 2014, 2016, 2018 & 2019). Time series and diurnal trends of organic and inorganic aerosols (OA and IA, respectively) were analysed. Over all seasons OA had a higher contribution (60-80 %) to total submicron (diameter less than 1  $\mu$ m) particular matter (PM<sub>1</sub>) than IA (NO<sub>3</sub>= 3-12%, SO<sub>4</sub>= 4-20%, NH<sub>4</sub>= 3-21% and Chl = 0.2-0.4%). During summers of the years 2013, 2016 and 2018 OA had a higher contribution to PM<sub>1</sub> compared to spring and autumn seasons. Meantime in 2014 and 2019 the highest contribution of OA was observed over the spring seasons.

Diurnal trends of OA and IA were assessed in order to characterise possible day and night aerosol chemistry and sources. Diurnal trend of OA showed a higher mass concentration during morning hours (5-7 h) and lower mass concentration during daytime (13-19 h). Similar trend was observed for NO<sub>3</sub> mass concentration, which reached maximum between 5-7 h and minimum between 15-20 h. Mass concentrations of SO<sub>4</sub> and NH<sub>4</sub> were lower during daytime (10-19 h and 13-23 h, respectively) compared to night time (1-6 h and 1-10 h, respectively). Formation of SO<sub>4</sub> aerosol was possibly occurring during daytime by the oxidation of gaseous precursor SO<sub>2</sub> followed by particle formation through nucleation and condensation processes, whereas significantly higher SO<sub>4</sub> concentration between organics and sulphates were analysed and indicated that there is no special connection between higher m/z signals with SO<sub>4</sub> in Rūgšteliškis rural environment. The results of this study could provide a better understanding regarding climate changes on local and global scale.

Keywords: Aerosols, Chemical composition, Particular matter, Submicron particles

### **INTRODUCTION**

Aerosol particles are ubiquitous in the atmosphere and have a great influence on the air quality based on their chemical composition and cause environmental changes [2]. Chemical composition of these particles varies depending to their sources and formation mechanisms. Moreover, chemical composition of aerosol particles impacts their properties such as radiative forcing, hygroscopic properties, reactivity, capacity to create cloud beads and other. Thus, their impacts vary from visibility reduction fog formation and precipitation; solar radiation reduction; temperature and wind distribution alteration; effects on materials; effects on vegetation. Moreover, they specifically effect human health which includes: declined in lung function; increased respiratory symptoms such as cough, shortness of breath, wheezing and asthma attacks; chronic obstructive pulmonary disease; cardiovascular diseases; lung cancer [3] [4].

Several long-term studies of aerosol chemical composition in boreal forests were reported by Helmi et al. (2020), Heikkinen et al. (2020), Ivan et al. (2013). Helmiet al. (2020) expressed their work on long-term study of the regular changes of PM<sub>1</sub> (particulate matter with aerodynamic diameter  $<1 \mu m$ ) mass concentrations which revealed that PM<sub>1</sub> mass concentrations were highest in summer (for different size classes). The second most elevated loadings were achieved in spring, which were 80-88 % of those in summer [5]. The lowest loadings were measured in autumn and winter, when the mass concentrations were 74-78% of those in summer. These findings showed that temperature had a strong influence on the measured PM<sub>1</sub> mass concentrations. In particular, the high late spring and summertime temperatures promote secondary organic aerosol (SOA) formation. Another study of submicrometer aerosol chemical composition and its trends between 2012 and 2018 in the boreal forest (Finland) by Heikkinen et al., (2020) demonstrated that higher contribution of inorganic aerosol species (50%) occurred in wintertime, while during the summer an increased level of organics (80%) were connected to biogenic SOA formation. Organic aerosol (OA) concentrations were up to 70% higher throughout warm months compared to cold months. The same study revealed that sulphate played important role in SOA formation [6]. Thus, a clear increase in PM<sub>1</sub> fraction was observed in boreal forests during the warm seasons, but yet the chemical reaction behind increased SOA formation remained poorly understood.

In order to deepen the understanding of role of each aerosol chemical component such as OA and IA (NO<sub>3</sub>, SO<sub>4</sub>, NH<sub>4</sub>, Chl) in the boreal forests, a study of long-term measurements in rural environment was performed. In our study, Aerosol Chemical Speciation Monitor (ACSM) measurement data were analysed to get more profound understanding about chemical species, their impact on the surroundings and climate change. The analysis focuses on assessment of chemical composition carried out in 3 seasons (spring, summer and autumn) of 5 years (2013, 2014, 2016, 2018 & 2019) in the Rūgšteliškis rural environment, Lithuania.

# **MEASUREMENT AND METHOD**

# **Description of measurement site**

The aerosol main chemical components were investigated in Rūgšteliškis (Lithuania) rural environment by using Aerosol Chemical Speciation Monitor (ACSM). The measurements were carried out in three seasons (spring, summer and autumn) of 5 years (2013, 2014, 2016, 2018 & 2019) at Aukštaitija integrated complex monitoring station (55°46'N, 26°00'E,160 m above Sea level, rural forested environment in Rūgšteliškis, Lithuania). This station is located in the north-eastern part of Lithuania, in remote forested Aukštaitija National park's area. Forests cover 70% of this area, mostly 60 years old in average pine (*Pinus sylvestris*) stands

and sparsely populated area with vegetation varied from steppe to tundra species. The measurements were taken at 1.5 m above the ground level. The climate can be described as middling cold with higher humidity and considerable rainfall. The nearest major city Utena is about 27 km to the south from Rūgšteliškis [7].



Fig. 1. Location of Rūgšteliškis sampling site, (Aukštaitija monitoring station) Lithuania [7].

# Instrumentation

The Aerosol Chemical Speciation Monitor (ACSM) (Aerodyne Research, Inc., Billerica, MA, USA) was deployed at Rūgšteliškis (Lithuania) site for the chemical characterization of non-refractory submicron particulate matter aerosol main components. ACSM is build for long-term measurements and routine monitoring applications [8]. The sampling aerosol flow of 1.6 lpm initially move across  $PM_{10}$  impactor-inlet (self-design), a 2.5 m vertical stainless steel sampling tube (6 mm inner diameter) and a Nafion dryer (MD-110-48S-4, Perma Pure LLC, Toms River, NJ, USA). Rough particles removed by the impactor whereas flow rate of 1.6 l/min minimized the particle transport losses in the particle size range from 30 nm to 1 µm and relative humidity lower than 50% set by dryer. It was estimated that less than 2% particles were loses in the line.

The aerosol particles reaching the ACSM were focused into a resistively heated surface at 600 °C, where the non-refractory PM<sub>1</sub> components were flash vaporized. Consequently, the resulting gases were revealed and chemically analyzed with 70 eV electron impact quadrupole mass spectrometer. The operation of instrument occurred with a time resolution of 30 min for typical aerosol loadings (several  $\mu g \cdot m^{-3}$ ) with a scan rate of mass spectrometer at 220 ms · amu<sup>-1</sup> from m/z 12 to 149. The mass concentrations and mass spectra were processed via ACSM standard data analysis software (v 1.5.3.0) and DAQ 1.4.4.4. The mass concentration under ambient conditions were measured with a detection limit <0.2  $\mu g \cdot m^{-3}$  for organic matter (OM), sulphates (SO<sub>2</sub><sup>-4</sup>), nitrates (NO<sup>-3</sup>), ammonium (NH<sup>+4</sup>) and chlorides (Cl<sup>-</sup>). The instrument was periodically maintained and calibrated using ammonium sulphate (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> and ammonium nitrate (NH<sub>4</sub>NO<sub>3</sub>) [7].

# Calculation of aerosol acidity

Aerosol acidity was assessed based on the ratio between measured ammonium concentration (NH<sub>4</sub>) and the theoretically predicted concentration of ammonium (NH<sub>4</sub>,<sub>predict</sub>) needed to neutralize the inorganic anion mass concentrations measured by the aerosol mass spectrometer. NH<sub>4</sub>,<sub>predict</sub> was evaluated as following:

$$NH_{4 \text{ predict}}^{+} = 18X \frac{SO_{4}^{2^{-}}}{96} \times 2 + \frac{NO_{3}^{-}}{62} + \frac{CI^{-}}{35.5}, \qquad (1)$$

where  $NH_4^+$ ,  $SO_4^{2-}$  and  $Cl^-$  are measured mass concentrations ( $\mu g m^{-3}$ ).

# **RESULTS AND DISCUSSION**

### **Overview of different years tendencies**

The different tendencies of aerosols chemical compositions were observed throughout all the three seasons (spring, summer and autumn) of the five years (2013, 2014, 2016, 2018 and 2019) (Fig 2). The obtained results indicated that the highest contribution to total submicron particular matter (PM<sub>1</sub>) had organic aerosols (OA). The contribution of organic aerosols to total PM<sub>1</sub> varied between 60% and 80%. Contribution of OA in spring was observed (between 72% and 79%), summer (between 67% and 81%) and autumn (between 60% and 68%). Data indicates that during summer of 2013, 2016 and 2018 OA had a higher contribution to PM<sub>1</sub> compared to spring and autumn. Meantime in 2014 and 2019 the highest contribution of OA was observed over the spring.

IA were showing lower contribution 20-40% (NO<sub>3</sub> = 3-12%, SO<sub>4</sub> = 4-20%, NH<sub>4</sub> = 3-21% and Chl = 0.2-0.4%) over all seasons. During 2014 the highest contribution of NH<sub>4</sub> and SO<sub>4</sub> was observed (on average 17% and 12%, respectively). Whereas during all 3 seasons in 2018 a higher contribution of NO<sub>3</sub> was observed (on average 11%). These results indicate that sulphate, nitrate and ammonia changes from year to year but not related to seasonality.



Fig. 2. Main aerosol chemical composition of three seasons (spring, summer and autumn) in the year 2013, 2014, 2016, 2018 and 2019.

# **Diurnal trends**

For all measurement campaign data diurnal plot analysis of OA and IA were assessed (Fig 3) in order to characterise possible day and night aerosol chemistry and sources. Higher mass concentration of OA was observed during morning hours (5-7 h) while lower mass concentration was registered during a daytime (13-19 h) (Fig 3A). Similar trend was observed for NO<sub>3</sub> mass concentration, which reached maximum between 5-7 h and minimum between 15-20 h (Fig 3B). These trends remained unchanged during different seasons and years. This diurnal pattern possibly indicates nocturnal chemistry. Furthermore, similar diurnal patterns of NO<sub>3</sub> and OA show a possible connection between these two chemical compounds. In agreement, Xu et al. (2015) reported that NO<sub>3</sub> chemistry could play a key role in production of biogenic SOA at night. In addition, Lee et al. (2016) suggested that organic nitrates can be a significant contributor to biogenic secondary organic aerosols mass produced via night time NO<sub>3</sub> chemistry. Thus, a possible link between OA and NO<sub>3</sub> in rural environment was observed.

NH<sub>4</sub> had lower mass concentration during daytime (13-23 h) and higher mass concentration during night time (1-10 h). It was observed that ammonia did not show any clear diurnal pattern (Fig 3D). According to Allen et al. (2019) ammonium aerosol occurs in the form of ammonium nitrate (NH<sub>4</sub>NO<sub>3</sub>) and ammonium sulphate ((NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>) which are formed by the neutralization of nitric acid (HNO<sub>3</sub>) and sulphuric acid (H<sub>2</sub>SO<sub>4</sub>) with ammonia. Therefore, it is likely that ammonium is used to reduce the acidity of SO<sub>4</sub>, NO<sub>3</sub> and Chl and formation of other aerosols as a result rather low concentration of ammonium is present in our study.

SO<sub>4</sub> had lower mass concentration during daytime (10-19 h) and higher mass concentration during night time (1-6 h) in spring, summer and autumn (Fig 4 C). Formation of SO<sub>4</sub> aerosol was possibly carried out during day time by the oxidation of gaseous precursor SO<sub>2</sub> followed by particle formation through nucleation and condensation processes. Therefore, significantly higher SO<sub>4</sub> concentration was observed during the day time. While several studies showed a possible link between NO<sub>3</sub> and OA, but a possible connection between SO<sub>4</sub> and OA remained poorly investigated. Therefore, additional analysis of SO<sub>4</sub> was performed and presented in 3.3 section. Riva et al. (2019) studies in (Helsinki) Finland indicated that possible connection between SO<sub>4</sub> and OA because the area was influenced by Smelters and refineries that emitted large amounts of SO<sub>2</sub> originated from Russia (Kola peninsula) whereas in our study the situation was quite different therefore there was no special connection between OA and SO<sub>4</sub> observed [9]. Therefore, in this study results indicate that sulphate has very different origin than NO<sub>3</sub> and NH<sub>4</sub>.



Fig. 3. Five years diurnal trend of (A) OA, (B) NO<sub>3</sub>, (C) SO<sub>4</sub> and (D) NH<sub>4</sub> for three seasons (spring, summer and autumn).

### The relationship between organic and sulphate

In order to investigate a possible connection of sulphate and OA in rural forestry environment, an additional analysis of intensity of higher m/z signals and sulphate levels was performed. Ambient observations of the relative intensity of organic fragments with >m/z85 as a function of sulphate was analysed. Sum of >m/z85 signals intensity normalized to OA mass concentration (>m/z85/Org) was chosen as a proxy of presence of low volatile oligomers in SOA. In recent studies Riva et al. (2019) observed that there was a connection between higher m/z signals of OA with sulphate in rural forest environment due to sulphate emission (from smelters and refineries). The same study showed that low volatile oligomers play important role in a boreal forest and are directly connected to heterogeneous SOA transformations. In addition, sulphate likely cause aerosols to be fairly acidic. Thus, in our study we compared >m/z85 with OA and SO<sub>4</sub> mass concentrations together with aerosol acidity (Fig 4).



Fig. 4. Ambient observations of organic fragments with >m/z85 normalized to organics with SO<sub>4</sub> in the year 2013, 2014, 2016, 2018 and 2019. Bigger points presentless acidic aerosols. Colour plot shows mass concentration of OA.

As it is presented in Fig. 4, sum of >m/z85/Org signals intensity decreased with increasing SO<sub>4</sub> mass concentration. The same tendency was observed for all five years of study. The values of correlation coefficient between >m/z85/Org and SO<sub>4</sub> during all five years varied between r=-0.40 and r=-0.30, indicating no significant link between these parameters. These results suggest that no low volatile oligomers formed from heterogeneous processes were associated with increased levels of sulphate. Thus, sulphate likely had no significant influence on heterogeneous transformations of SOA.

In addition, in Fig. 4 points size presented acidity of aerosols. As a proxy of aerosol acidity parameter of NH<sub>4 meas</sub>/ NH<sub>4 neu</sub> was used. Here higher values of NH<sub>4 meas</sub>/NH<sub>4 neu</sub> were associated with lower aerosol acidity. During all measurement campaigns, higher aerosol acidity occurred with higher SO<sub>4</sub> mass concentration proving that sulphate had an impact on aerosol acidity features. Thus, while SO<sub>4</sub> did not show link with low volatile oligomers, it was connected with aerosol acidity. OA mass concentration was compared with above analysed parameters (>m/z85/Org, SO<sub>4</sub> mass concentration and NH<sub>4 meas</sub>/NH<sub>4 neu</sub>). It was estimated that the highest mass concentration of OA was associated with intensities of smaller than m/z85 signals, more acid aerosols and higher SO<sub>4</sub> mass concentration. A moderate correlation between OA and SO<sub>4</sub> mass concentrations (which varied between r = 0.46 and r = 0.66) was likely caused by atmospheric conditions (such as atmospheric mixing height, temperature, wind speed and other) rather than interconnections between these chemical species.

### CONCLUSIONS

In this work aerosol main chemical compositions were investigated in Rūgšteliškis (Lithuania) rural environment. The analysis of five years (2013, 2014, 2016, 2018 and 2019)

data series was performed for three seasons (spring, summer and autumn). Time series and diurnal trends of organic aerosols (OA) and inorganic aerosols (IA) were analysed. OA were exhibiting higher contribution of 60-80% to total submicron particular matter (PM<sub>1</sub>) and this contribution was higher in spring and summer and lower over in autumn. IA showed lower contribution to PM<sub>1</sub> (20-40%) (NO<sub>3</sub> = 3-12%, SO<sub>4</sub> = 4-20%, NH<sub>4</sub> = 3-21% and Chl = 0.2-0.4%) over all three seasons. During 2014 a higher contribution of NH<sub>4</sub> and SO<sub>4</sub> (21% and 14%, respectively) was observed. Whereas during 2018 there was a significant increase in contribution of NO<sub>3</sub> (12%). These results indicate that concentration of sulphate, nitrate and ammonia changes from year to year but not because of seasonality.

The day and night chemistry were analysed based on diurnal patterns of OA and IA. OA and NO<sub>3</sub> exhibit higher mass concentration in the morning than evening hours and did not depend on the seasons and years. The NO<sub>3</sub> mass concentration was higher 5-7 h and lower between 15-20 h and this diurnal trend were similar for three different seasons (Spring, summer and Autumn) of five years (2013, 2014, 2016, 2018 and 2019). Therefore, this trend phenomenon indicatednocturnal chemistry. In addition to that it was observed that this similar diurnal trend of NO<sub>3</sub> and organic aerosols have a possible connection with each other. Previous studies of Xu et al. (2015) supported this connection by stating that biogenic SOA production at night carried out by NO<sub>3</sub> and organic NO<sub>3</sub> chemistry. Thus, a possible association was observed between OA and NO<sub>3</sub> in Rūgšteliškis rural environment.

 $SO_4$  showed lower mass concentration during daytime than night time in spring, summer and autumn. An additional study of  $SO_4$  role in rural environmental showed that  $SO_4$  was associated with more acid aerosol but did not have significant influence on heterogeneous transformations of SOA.

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