

5th INTERNATIONAL SCIENTIFIC CONFERENCE

CHEMICAL TECHNOLOGY AND ENGINEERING

PROCEEDINGS



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UKRAINE, LVIV, JUNE 23-26th, 2025

Ministry of Education and Science of Ukraine
Lviv Polytechnic National University

**5th International Scientific Conference
«Chemical Technology and Engineering»**

P R O C E E D I N G S



Ukraine, Lviv, June 23-26th, 2025

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The Conference Organizers:

Department of Chemical Engineering, Institute of Chemistry and Chemical Technologies,
Lviv Polytechnic National University (Lviv, Ukraine);

Łukasiewicz Research Network – New Chemical Syntheses Institute (Pulawy, Poland);

Faculty of Chemical and Process Engineering, Warsaw University of Technology (Warsaw,
Poland);

Department of Informatics and Environment Quality Research, Faculty of Building Services,
Hydro and Environmental Engineering, Warsaw University of Technology (Warsaw, Poland);

The Nice Institute of Chemistry, Université Côte d’Azur (France);

Scientific Society of Students, Doctoral Candidates and Young Researchers of Lviv
Polytechnic National University (Lviv, Ukraine);

Alumni Association of Lviv Polytechnic National University (Lviv, Ukraine);

Western Scientific Center of National Academy of Sciences of Ukraine and Ministry of
Education and Science of Ukraine (Lviv, Ukraine).

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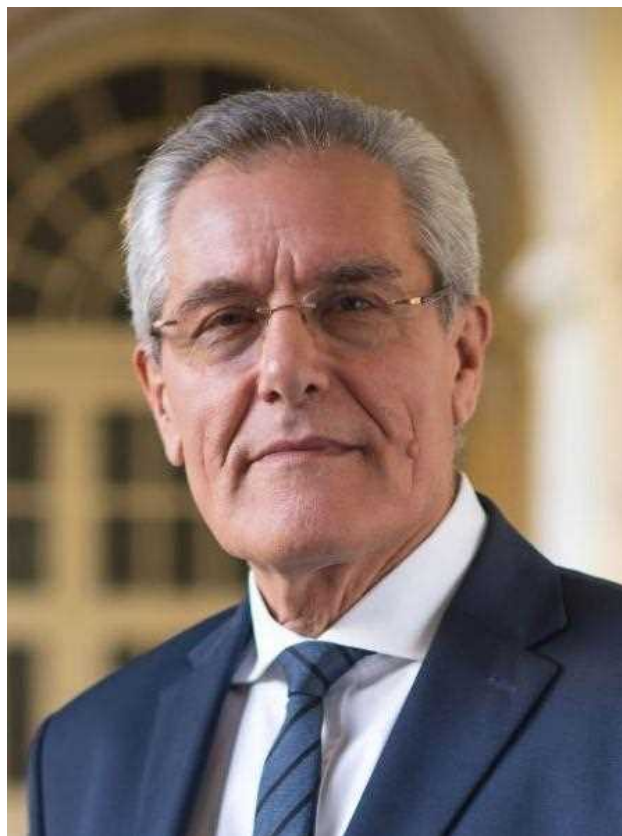
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Greetings from the Program Committee's Chairman of
5th International Scientific Conference «Chemical Technology and Engineering»,
Rector of Lviv Polytechnic National University in 2007–2025, DSc, Professor
Yuriy Bobalo



Dear participants!

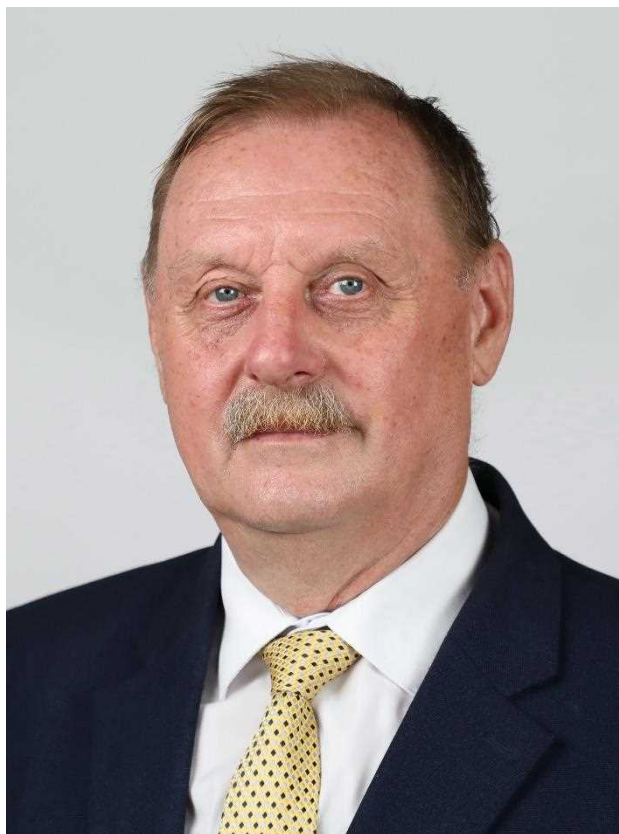
Lviv Polytechnic National University is pleased to welcome you to the 5th International Scientific Conference «Chemical Technology and Engineering» (CTE-2025)!

This year's Conference takes place during a difficult time for Ukraine, which continues to defend its freedom – the freedom to choose, to preserve identity, and to develop science – in the face of the ongoing russian invasion. Despite these challenges, we remain committed to uniting the scientific community.

The Conference CTE-2025 is an opportunity to demonstrate solidarity, exchange knowledge, share experience and best practices, and affirm that science endures even in times of crisis.

I wish all participants fruitful work and new achievements in the field of chemical technology and engineering!

Greetings from the Organizing Committee's Chairman of
5th International Scientific Conference «Chemical Technology and Engineering»,
Head of Department of Chemical Engineering,
Lviv Polytechnic National University, DSc, Professor
Volodymyr Atamanyuk



Dear colleagues!

I am delighted to welcome you to our traditional conference, dedicated to current issues of chemical technology and engineering.

This year, we meet online due to ongoing challenges – both global and national. Forty months after the full-scale russian invasion, Ukraine continues its struggle for freedom. Now, thanks to modern technology and the efforts of the Organizing Committee, we are still able to unite the scientific community.

The Conference remains an important platform for knowledge exchange, scientific cooperation, and building strong professional connections in chemical, food, and biotechnologies, green chemistry, and ecology.

I wish you all fruitful work, engaging discussions, and new scientific achievements – and I truly hope our next meeting will take place in a peaceful and free Ukraine.

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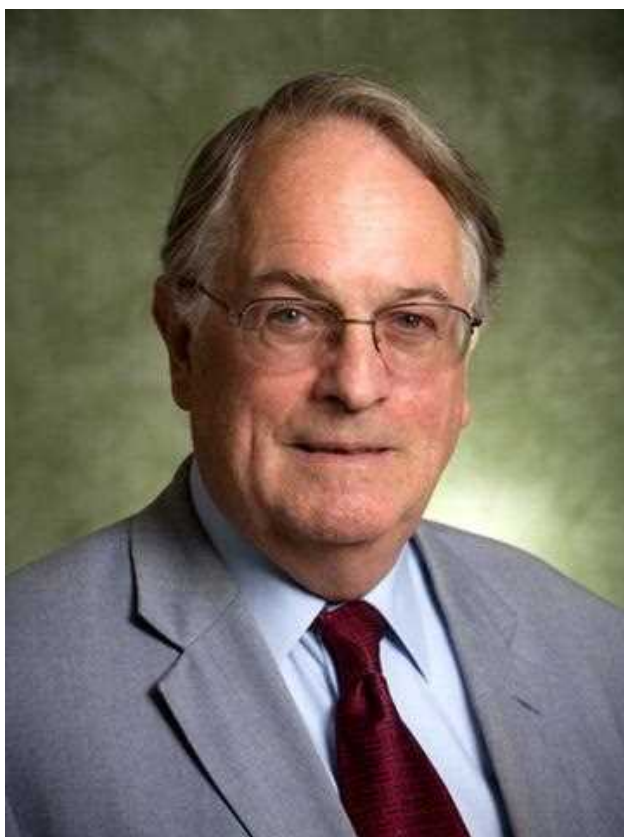
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PLENARY PRESENTATIONS



Professor

M. Stanley Whittingham

2019 Nobel Prize Laureate,
SUNY Distinguished Professor,
Member of National Academy of
Engineering, Director of NECCES,
Binghamton University (SUNY),
USA



**BROKEN CLIMATE SYSTEM:
WHO IS RESPONSIBLE, HOW WE
KNOW AND WHY WE NEED
CLIMATE RESILIENT
DEVELOPMENT FOR SURVIVAL**

Doctor Svitlana Krakovska

PhD, Member of Intergovernmental
Panel on Climate Change (IPCC),
Head of the Laboratory of Applied
Climatology of Ukrainian
Hydrometeorological Institute of SESU
and NASU,
Senior Researcher of National Antarctic
Research Center of MESU,
Ukraine



**RESEARCH INTO INNOVATIVE
ENERGY CARRIERS FOR THE
RENEWABLE ENERGY SYSTEM**

Professor Viktor Hacker

DSc, Professor, Head of the Institute of
Chemical Engineering and
Environmental Technology,
Graz University of Technology,
Austria



**DRIVING EFFICIENCY AT THE
MICRO SCALE: PROCESS
INTENSIFICATION THROUGH
MODEL-BASED DESIGN**

Professor **Igor Plazl**

DSc, Professor, Member of the
European Federation of Chemical
Engineering (EFCE) – WP on Process
Intensification and CAPE-WP, Head of
the Chair of Chemical Process,
Environmental, and Biochemical
Engineering,
University of Ljubljana,
Slovenia



**BIOBASED EPOXY RESINS AND
COMPOSITES FOR SPACE
APPLICATIONS**

Professor **Alice Mija**

DSc, Professor, The Nice Institute of
Chemistry, Université Côte d'Azur,
France



**SPEEDING UP GREEN ENERGY
TRANSITION THROUGH
DEVELOPMENT OF SMART
ENERGY SYSTEMS**

Associate Professor **Goran Krajačić**

PhD, Associate Professor, European
Sustainable Energy Innovation Alliance
(ESEIA), Faculty of Mechanical
Engineering and Naval Architecture,
University of Zagreb,
Croatia

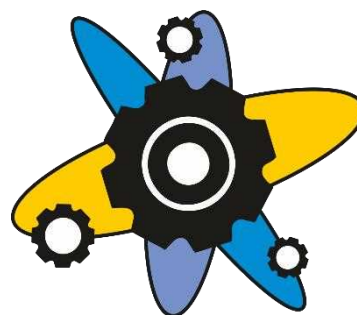


**ALTERNATE SOLID FUEL BASED
ON SECONDARY RAW
MATERIALS**

Associate Professor
Oleksandr Ivashchuk

DSc, Associate Professor,
Deputy Director for Scientific and
Educational Work at Institute of
Chemistry and Chemical Technologies,
Associate Professor of the Department
of Chemical Engineering,
Lviv Polytechnic National University,
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THE CONFERENCE'S ORGANIZERS



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1949

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Department of Chemical Engineering of Lviv Polytechnic National University originates from 1949. Research of the Department of Chemical Engineering have been formed into a scientific school of mass transfer in systems with solid and liquid phases, study of the treatment processes of gas and liquid environments of solid impurities, mathematical and computer modeling of the basic processes of chemical technology.

The Department provides training of specialists in «Equipment of chemical industries and enterprises of building materials», «Processes and equipment of chemical plants», and «Computer chemical engineering».

In recent years, the Department has been actively developing a new line of work that is associated with numerical modeling of chemical technology processes. Using advanced software for CFD modeling, the Department prepares solid 3D models of the objects with visualization of the research results in the form of change of the field of experimental values, trajectory of phase flows, graphs, tables, etc.

CFD simulation covers the full range of tasks that arise in the design, modernization, and analysis of the equipment of chemical, food, pharmaceutical industries, and the building materials industry.

Areas of research projects

- solid materials drying
- filtration drying of the porous and dispersed materials
- spray drying of solutions, suspensions and pastes
- cleaning of gas emissions of dust and the gas separation of heterogeneous systems
- processing of dispersed materials in swirling flows (drying, annealing, chemical treatment)
 - optimization of heat in industrial processes
 - optimization of hydrodynamics and heat transfer in industrial installations – designing of the technology systems (software simulation: SOLIDWORKS, ANSYS FLUENT)
- CFD modeling



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Łukasiewicz Research Network – New Chemical Syntheses Institute (Sieć Badawcza Łukasiewicz – Instytut Nowych Syntez Chemicznych) seated in Puławy, Poland, is a state research institute with a long lasting tradition and well known trade mark. Since 2019, it has been a part of the Łukasiewicz Research Network.

The principal goal of the Institute is to increase the competitiveness of chemical companies operating in the inorganic chemicals mostly mineral fertilizers production sectors through developing innovative technologies, services and products. Łukasiewicz – INS carries out research and development works in a close partnership with industry employing highly qualified staff and maintaining the highest standards, with respect to research methods and procedures. It has the unique advantage of carrying out research works in pilot plants under real operating conditions. The Institute co-operates with all fertilizer producers in Poland and many abroad. This fruitful cooperation resulted in numerous licenses sold i.e. to Germany, Bulgaria, Czech Republic, Croatia, Ukraine and Hungary. Our catalysts are purchased worldwide by a number of countries, including Colombia, Chile, and USA.

In recent years, Łukasiewicz – New Chemical Syntheses Institute has developed ‘green’ competences in the field of bioeconomy such as supercritical CO₂ extraction of plant raw materials, biodegradable polymers or environmentally friendly smart fertilizers.

Research and technologies

- production and purification of syngas, H₂, CO₂ including the use of decarbonised gases in energy transformation (production, purification and management of biohydrogen and biomethane obtained from biogases)
- technologies regarding ammonia, nitric acid and its salts
- technologies for reduction in emissions of nitrogen oxides
- catalysts, sorbents and inert materials
- green hydrogen
- mineral fertilizers and mineral-organic fertilizers
- supercritical extraction of natural raw materials
- unit operations: granulation, absorption, adsorption, crystallization, filtration
- management of organic waste: digestates, sewage sludge from municipal and industrial wastewater treatment plants
- biodegradable plastics
- phosphate, polyphosphates, phosphoric acid and polyphosphoric acid technologies
- inorganic sodium salts technologies and peroxide compounds technologies

Research services

- technical assessment of industrial plants
- chemical process design
- expert opinions (fertilizer and inorganic industries)
- micronization
- chemical analyses, environmental research

Experimental production

- catalysts and sorbents
- hop pellets and hop extracts
- bioactive extracts from plants
- chemicals for fertilizer conditioning, steel degreasing and steel phosphating



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The Faculty of Chemical and Process Engineering, Warsaw University of Technology (FCPE WUT) is the leading academic entity in chemical engineering in Poland, known for high quality in scientific research and student education (B.Sc.Eng., M.Sc., and Ph.D.). In 2022,

following the nationwide academic evaluation process (PKA), the Faculty obtained the distinction "The Excellence in Academic Education".

The academic staff of FCPE WUT is formed by 48 persons, with 7 full professors and 10 university professors. Five professors are members of the European Federation of Chemical Engineering (EFCE), and seven professors are members of the Committee of Chemical and Process Engineering of the Polish Academy of Sciences. The Dean of the Faculty in 2020-2024 is prof. Marek Henczka.

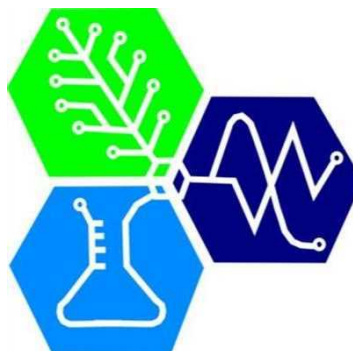
The structure of the Faculty includes one chair (*Chair of Dispersed Systems Engineering*) and four departments of: (i) *Chemical Reactors Engineering and Dynamics*, (ii) *Intensification of Industrial Processes*, (iii) *Process Kinetics and Thermodynamics*, and (iv) *Biotechnology and Bioprocess Engineering*.

Several specialized laboratories are operating within the FCPE WUT:

- Aerosol Filtration Laboratory (*AEROFIL*, led by dr Anna Jackiewicz-Zagórska)
- Laboratory of Medical Aerosols and Inhalers (*RESPI-LAB*: prof. Tomasz Sosnowski)
- Biomedical Engineering Laboratory (*BIOMED-LAB*: prof. Tomasz Ciach);
- Laboratory of Multifunctional Emulsion Systems (prof. Ewa Dłuska)
- Product Engineering Laboratory, including the Graphene Lab (prof. Łukasz Makowski)
- High Pressure Processing Laboratory (prof. Marek Henczka)
- Membrane Technology Laboratory (prof. Maciej Szwał)

Scientific activities of the Faculty are also related to:

- nanotechnology and functional materials,
 - process intensification (supercritical technology, microwave-assisted processes, high-performance dispersion and mixing, etc.),
 - processes for the environment and sustainability,
 - experiments and computer simulations of fluid flows, heat and mass transfer, chemical reactors and bioreactors,
- and other fundamental and technological problems.



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The Department was established in 2007, as a result of a change in the organizational structure of the Faculty of Environmental Engineering of the Warsaw University of Technology, by merging the Department of the Application of Mathematical Methods and Department of Environmental Chemistry. Currently the activities of the Department are carried out in three main areas around which there are teams concentrated at:

1. Environmental Informatics and Environmental Protection Management
 - a. Environmental Informatics deals with the research and development of methods for creating, transmitting, storing, processing, modeling, interpretation, presentation and dissemination of data and information for solving environmental problems in the process of investment preparation and implementation. Environmental Information Technology is also used to support environmental management in industrial activities, including the impact of rational use of energy, water, raw materials, waste management and emission control in the production process on the competitiveness of the product on the market;
 - b. Environmental Protection Management is conducted both at the level of management in the processes of infrastructure development, management in enterprises, as well as management in local governments units, with particular emphasis on urban agglomerations. It includes the preparation of Strategic Environmental Assessments for policies, plans and programs as well as Environmental Impact Assessments for different projects. The activities of the Department are also related to the nature of social conflicts resulting from the development of infrastructure, design and implementation of social consultancy programs accompanying the procedures of preparation of investments implementation, as well as protection of residents against various nuisances of the urban environment.
2. Statistics and Remote Research of the Environment

- a. Statistics and Geostatistics are modern methods of classical and spatial statistics used to solve various problems related to environmental research, including those regarding cost reduction and rationalization of these surveys. The research area of the Team is exploratory analysis of environmental data: studies of variability and spatial correlation, methods of estimation and simulation of spatial distributions, optimization of measurement networks, resource estimation, uncertainty assessment. In particular, the Team's interests include the issue of spatial integration of various environmental data;
 - b. Remote Research of the Environment uses various types of satellite images from different types of satellites to observe the Earth's surface, for example, soil moisture or changes in the forest cover. Remote tests are used for quick monitoring of large areas, which would be almost impossible to test using classical measurement methods.
3. Environmental Chemistry
- a. Water and Wastewater research include chemical tests of waters, sewage and sludge in the scope of basic pollution indicators, research on methods of removing hard-to-decomposable, toxic, anthropogenic organic pollutants from sewage, based on highly efficient oxidation processes and electrooxidation;
 - b. Metals Research in the Environment includes determination and speciation of metals in water, sewage, bottom sediments, soil and atmospheric air, testing of metal migration in all elements of the environment, including penetration of metals into plants;
 - c. Research on Organic Micropollutants includes determination of microgram, anthropogenic, water pollution, sewage, sediments and soils (petroleum hydrocarbons, PAHs, polychlorinated biphenyls and organotin compounds).

There are currently 20 people working at the Department. The academic staff include 1 full professor, 2 associate professors, 7 assistant professors and 2 assistants. In addition the Department employs 4 senior lecturers and 4 administrative and technical employees.



Nice Institute of Chemistry (ICN), Côte d'Azur University

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The Nice Institute of Chemistry (ICN), directed by Professor Uwe J. Meierhenrich, is a research laboratory at Université Côte d'Azur associated with CNRS (UMR 7272). The ICN is organized in different research teams on thematic comprising Simulations, Perfumes, Flavors, Cosmetics, Evolution, Synthesis, Perfumes, Industry, Catalysis, Environment, Bioactive Molecules, Molecular Diversity, Metabolomics, Human and Environmental Radiochemistry, and Eco-Compatible Materials and Polymers. The ICN also hosts a technology platform, made up of three joint services (NMR, mass spectrometry and molecular modelling).

The ICN has a total of 41 permanent staff including 6 CNRS researchers (2 senior researchers, 4 researchers), 26 faculty members (7 full professors, 19 associate professors), 5 technical staff (2 senior research officers, 1 research officer and 2 technicians) and 4 administrative staff. We also have 13 non-tenured staff (2 emeritus professors, 2 seconded associate professors, 3 honorary researchers, 6 postdocs) and 32 doctoral students.

The ICN has a total of 91 publicly funded and competitively tendered institutional contracts: 2 European FP7 projects and 1 H2020 project, coordination of 2 international ANR (French National Research Agency) grants, participation in 2 Euro-Mediterranean projects and involvement in 8 Hubert Curien programs. In addition, we participate in 18 national ANRs (including coordinating 2), 1 PIA (Program for Investments in the Future) project, 2 FUI (French Interministerial Funds), 2 ARC Foundation, 1 FRM (Foundation for Medical Research) and 1 INCA (National Cancer Institute) as well as 2 Matwin (Maturation & Accelerating Translation With Industry). The ICN participates in or has participated in 3 COST (European Cooperation in Science and Technology), 2 EU Projects (Marie Curie Actions), 1 ECOS North (Mexico), 1 ERANET ARIMNET (Coordination of Agricultural Research in the Mediterranean) 2016-19, 5 GDR (Groupements de Recherche), the CNRS ZATU network (Zone Atelier Territoires Uranifères), ToxNuc network, CEA (Alternative Energies and Atomic Energy Commission), nuclear toxicology.



Lviv Polytechnic National University

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Scientific Society of Students, Doctoral Candidates and Young Researchers of Lviv Polytechnic National University (SSSD) originates from 2005.

The purpose of SSSD activity is to protect the rights and interests of students, postgraduates, doctoral students, and young scientists studying or working at Lviv Polytechnic National University. SSSD supports scientific training, development of scientific ideas, innovations, and exchange of knowledge; promotes the scientific, inventive, and creative activities of young scientists, the disclosure of their scientific and creative potential, the development of scientific thinking, research skills, and innovative activities.

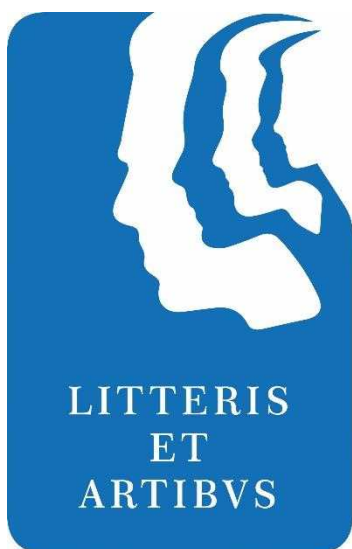
SSSD operates on the principles of freedom of scientific creativity; voluntariness, collegiality, openness; equality of the right of students, postgraduates, doctoral students, and young scientists to participate in the activities of SSSD.

Functions of Scientific Society of Students, Doctoral Candidates and Young Researchers

- conducting organizational, scientific, and educational events;
- popularization of scientific activity among student youth, distribution of information about scientific activities of higher educational institutions, scientific organizations, and institutions of Ukraine and other countries among persons studying and working at the University;
- conducting research contests for scholarships and other incentive measures to stimulate scientific research of persons studying and working at the University;

- representation of the interests of students, postgraduates, doctoral students, and young scientists in matters of scientific work and academic career development;
- improving the quality of scientific research;
- promoting the protection of the intellectual property of students, graduate students, doctoral students, and young scientists;
- preservation of information exchange between young scientists;
- cooperation and coordination of activities with scientific societies of students and young scientists of other higher educational institutions, promoting the development of inter-university and international cooperation.

SSSD cooperates with the administration of Lviv Polytechnic, student self-government bodies of the University, scientific and research institutions, state bodies of Ukraine, local self-government bodies, public and commercial organizations of Ukraine and other countries, whose activities do not support the principles of SSSD.



Асоціація випускників Львівської політехніки

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Alumni Association of Lviv Polytechnic National University is a community of alumni dedicated to serving their university, supporting charitable initiatives to develop the university's material and technical facilities, scholarship programs for talented students, researchers and teachers.



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The Western Scientific Centre of the National Academy of Sciences of Ukraine and the Ministry of Education and Science of Ukraine is the basic organizational and active part of the regional scientific, technical and innovative activity system in the West of Ukraine. It was created in 1971 for the consolidation of scientists in solving the main socio-economic and cultural problems of the region.

For the time of its functioning a number of research institutes have been created and scientific schools in Material Science, Mathematics, Geology, Biochemistry and Social Sciences have been established. The Centre focuses its attention on the solution of actual socio-economic and cultural problems of the development of the region and on the creation of an innovation infrastructure which is based on advanced achievements of Ukrainian science. For this purpose it has such an organizational structure which promotes an effective use of the scientific potential and cooperation of research institutions on the whole territory of Western Ukraine.

The supreme directing body is the Council which includes heads of the largest research institutes, of higher educational establishments, leading scientists and representatives of the regional and city authorities. The Western Scientific Centre conducts annual monitoring and analysis of research work in the region on the basis of which an information database has been created. It contains information on the scientific and research infrastructure of the western part of Ukraine, engineering and innovation proposals, the staff potential of the scientific institutions.

Among the priorities of the Western Scientific Centre we can mention:

- systems of management and ecological regulation of the region development; transborder cooperation and European integration;

- creation and mastering resource-saving and power-saving technologies in energetics, instrument-making and machine building;
- development and introduction of material strengthening technologies, methods of anticorrosion protection of pipelines;
- optimization of gas- and oil-extraction from the Pre-Carpathian deposits;
- the most efficient use and preservation of the natural resources of the Carpathians, of the Dnister, the Tysa and the Western Bug river basins;
- development and introduction of the information system of regional scientific centres;
- the study of the artistic monuments of the region, revival and preservation of handicrafts.

The above-mentioned directions are the key elements of the complex special programs creation concerned with innovative, scientific, technical, socio-economic developing of Ukraine with the assistance of Western Scientific Centre and its institutions including interregional collaboration in science and education.

COMPUTER SIMULATION IN THE CHEMICAL TECHNOLOGY AND ENGINEERING

Airflow and Mass Transfer Modeling as a Tool for Analyzing Drug Aerosolization and Delivery

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Abstract. *Chemical engineering methodology can be effectively used to solve problems of physiology, pharmacology, and medicine. Here, we present selected examples of such applications, focusing on numerical and experimental investigations of aerosol generation in inhalers of different types (e.g., dry powder inhalers, nebulizers) and particle dynamics during inhalation and drug deposition in different parts of the respiratory system. It is demonstrated how such an analysis helps to design more effective inhalers and pharmaceutical formulations for targeted and personalized drug delivery. Future directions of aerosol therapy with a potential input of chemical engineering are also proposed.*

Keywords: aerosols, CFD, medical applications, inhalers, mass transfer in the lungs.

Introduction

For several decades, chemical engineering researchers have expanded their research activities into several new areas related to the production and applications of new materials (including nanomaterials), the use of new energy sources, clean technologies, and health. The last direction has been driven by the recognition that the skills of chemical engineers as experts in the quantitative analysis of fluid flows, heat and mass transfer phenomena, and (bio)chemical kinetics can also be used to analyze physiological processes and design more effective drug delivery systems [1-3]. This direction of interdisciplinary development of chemical engineering was also reflected in the establishment of a scientific section within the European Federation of Chemical Engineering called “Chemical Engineering as Applied to Medicine” in 2022 [4].

Research on the application of aerosols, representing multiphase systems often used in medicine, has been carried out at the Department of Chemical and Process Engineering at Warsaw University of Technology for more than 20 years and continues to be developed in cooperation with pulmonologists and allergologists [5-7]. In this paper, we highlight the advantages of using engineering calculations and specialized experiments on anatomical models as tools to better understand the aerosolization process in inhalers and the subsequent aerosol flow, deposition, and physical interactions in different parts of the respiratory system. All of the presented materials demonstrate research conducted at CPE PW using chemical engineering methods and concepts.

CFD computations and *in vitro* experiments of particle flow and deposition in the selected regions of the respiratory system

The complexity of the respiratory system and the periodic flow of air during respiration present challenges for analyzing processes associated with medical applications of inhaled aerosols. CFD calculations performed for a simplified bronchial bifurcation geometry by Moskal and Gradoń [8] confirmed that inhaled aerosols are preferentially deposited in the area where the bronchus divides into two daughter tubes, but due to secondary flows and flow reversal during

expiration, additional hot spots appear. This was confirmed by *in vitro* experiments conducted on a physical model with exactly the same geometry as used in the calculations (Fig. 1). It is worth noting that even with this simple geometry, such experiments are not straightforward to perform, as they require reproducible generation of a stable aerosol with a particle size distribution typical of inhaled drugs, i.e., less than 10 μm in diameter. They also require reproduction of periodic breathing flow, which requires a special system (“artificial lung”). Finally, the deposition pattern in the model should be assessed either by direct visualization or more sophisticated quantitative analytical methods after the particles' recovery from individual parts of the model.

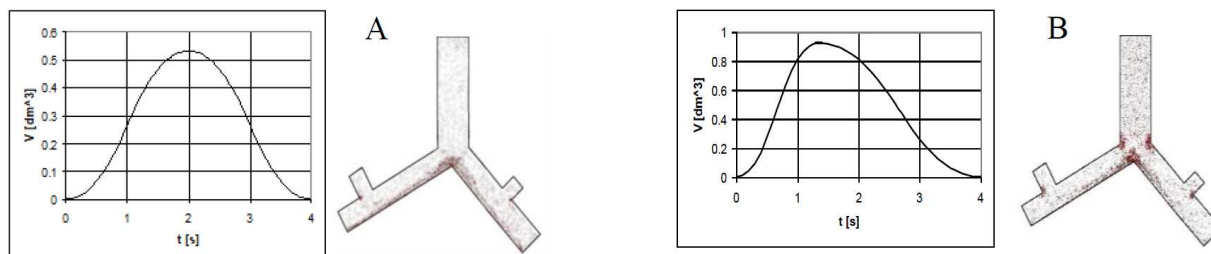


Fig. 1. Different local hot-spots of particle deposition in a model bronchial bifurcation at simulated symmetrical (A) and asymmetrical (B) breathing profiles.

Later works were related to the effect of the flow dynamics in the respiratory system in an anatomical replica of the oropharynx (oropharynx: OPX) region, using both CFD and experiments. These studies have shown that the commonly used averaged flow conditions are insufficient to reliably predict aerosol deposition [9, 10]. However, due to low computational cost, this simplification is still used, especially when CFD has to be used to model larger parts of the respiratory system [11].

Process intensification in aerosol generation and deposition for medical purposes

The particle size distribution of aerosolized drug powder depends on the properties of the powder (granulation, cohesiveness), inhaler design, and flow rate. The latter two factors determine the local aerodynamic stresses that ultimately lead to deagglomeration of the particles before they leave the inhaler. Of course, the aerodynamic resistance (pressure drop: Δp) corresponding to these stresses cannot be too high, since the energy to generate airflow comes solely from the patient's inhalation. Dry powder inhalers (DPIs) are characterized by intrinsic aerodynamic resistance, R_D (typical units: $\text{hPa} \cdot \text{min} \cdot \text{dm}^{-3}$), defined by Eq. 1:

$$R_D = \frac{\sqrt{\Delta p}}{Q} \quad (1)$$

and Q – the volumetric airflow rate. Inhalers with high R_D , which are better at deagglomerating powders into fine aerosol particles, are often difficult to use by patients with lung diseases who prefer low-resistance DPIs. Unfortunately, even at high flow rates, such DPIs do not always allow for the generation of aerodynamic stresses sufficient to deagglomerate powder particles. In such situations, some process intensification solutions based on principles known in chemical engineering applications can be proposed to improve particle deagglomeration without significantly increasing R_D . For example, the usefulness of flow focusing and aerosol flow fluctuations has been demonstrated [12]. The example shown in Figure 2 confirms that a reduction in median particle diameter can be achieved through airflow pulsation, improving aerosol penetration into the lungs. Current research of DPIs is concerned with analysis and improvement the device design to avoid too early powder fluidization and aerosol emission (when the energy of

inspiratory flow is weak) resulting in insufficient deagglomeration of the powder and, consequently, a low dose of drug delivered to the lungs [13, 14].

The benefits of process intensification have also been demonstrated in other medical applications of aerosols, for example, to improve mist deposition in the nasal cavity [15]. Fig. 3 shows the measured *in vitro* (in an anatomical model of the nose) increase in deposition of 2-10 μm droplets delivered from a medical nebulizer. Such an effect helps to treat allergic rhinosinusitis and other nasal diseases using nebulization.

The ongoing studies focus on a quite new application of aerosols in medicine that extends beyond the inhalation, trying to assess the possibility of using aerosols as a carrier of anticancer drugs to other body cavities [16].

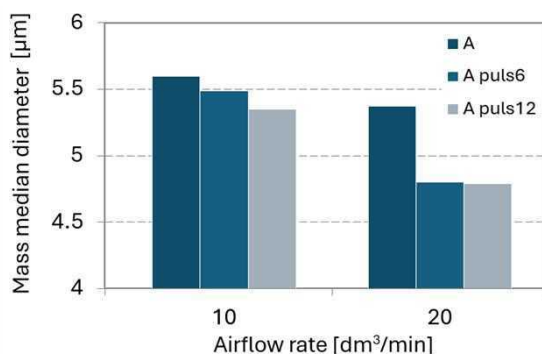


Fig. 2. Reduction of mass median diameter of aerosol particles due to deagglomeration in a convergent nozzle (type A) and pulsated flow with two frequencies ('puls6' and 'puls12').

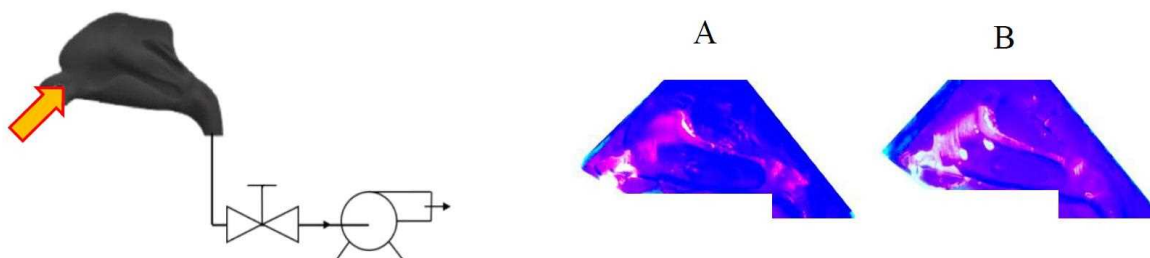


Fig. 3. Experimental system set-up and visualization of aerosol deposition pattern on the nasal surface (anatomical model): A – no pulsations, B – with ultrasonic pulsations.

Conclusions

This paper presents selected issues of aerosol generation and flow in both inhalers and the respiratory system. These processes can be studied using chemical engineering methods (mathematical modeling, including CFD, and experiments on anatomical models), leading to a better understanding of inhalation physiology and the prediction of clinical effects. Potential new applications for aerosols in medicine have been identified, which can be developed with considerable input from chemical and process engineering.

Acknowledgments

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Simulation of the Ultrafiltration Process: Modern Level and Development Trends

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Abstract. *The results of the analysis of the publications dedicated to the simulation of the ultrafiltration process during 2011-2020 are represented. The main trends in approaches to the simulation are defined.*

Keywords: ultrafiltration, membrane, pressure-driven processes, mathematical modeling, simulation

Introduction

The pressure driven membrane processes, including ultrafiltration (UF), are widely used in the chemical industry and related branches. At that, mathematical simulation is an important tool for the more effective application of these processes, including determining optimal and rational operation modes. Moreover, mathematical simulation methods are intensively developing in modern conditions. In the previous works, the attempts of generalization and systematization approaches to the simulation of the pressure driven membrane processes for 2000-2010 [1], reverse osmosis [2], and nanofiltration [3] for 2011-2020. The current work is the extension of these investigations. The purpose of the work is to analyze the main direction of the simulation of ultrafiltration during 2011-2020, the systematization and generalization of applied approaches, and also the determination of the rational range of the application of the different approaches to the simulation of UF. Also, the results of the generalization can be used as a starting point in choosing the strategy for the simulation of the specific UF process.

Materials and methods

As mentioned in previous works [1-3], the publications dedicated to the simulation of ultrafiltration in leading thematic journals were considered. Primarily, the journals dedicated to membrane processes such as the *Journal of Membrane Science* (Elsevier), and *Membranes* (MDPI) were analyzed, and also journals where the more general issues of chemical engineering and related branches, such as *Separation and Purification Technology*, *Desalination*, *Computers and Chemical Engineering*, *Chemical Engineering Journal*, *Chemical Engineering Research and Design*, (all Elsevier), *Water*, *Processes* (MDPI) *Chemical Engineering Transactions* (AIDIC) and others were also considered. The considered period is chosen according to considerations in the work [1], namely, it is the next decade after that considered in this work.

The classification of approaches to the simulation is based on the principles represented in the work [1]. In particular, the conventional methods (irreversible thermodynamics, diffusion, and pore flow) and the novel approaches (computational fluid dynamics (CFD), artificial neuron networks (ANN), and molecular dynamics, which is a newer method) were considered as well as the optimization and economical modeling. Taking into account the significant influence of concentration polarization on the ultrafiltration process, the simulation using the model of this phenomenon was also considered.

Results and Discussions

In work [2], except for the analysis of the simulation of the reverse osmosis process, the number of publications dedicated to the particular pressure driven membrane processes was represented. Among them, ultrafiltration (UF) was considered in more than 150 sources, which is

on the same level as forward osmosis (FO) and bigger than microfiltration (MF) and membrane bioreactors (MBR). However, it is significantly lower than reverse osmosis (RO) and nanofiltration (NF) (Fig. 1). In particular, in a review work [4], it was pointed out that the simulation was considered in 16.86% of articles dedicated to the ultrafiltration process published from 2009 to 2019. Among subtopics in the investigation of the considered process, the simulation was second after the issue of fouling (26.9%). Also, 8.24% of publications considered the optimization problems.

The distribution of publications by years is shown in Fig. 2. Unlike reverse osmosis and nanofiltration, for which the sustainable increase in the number of publications was observed [2, 3], in the case of ultrafiltration during almost all period under consideration the approximately constant number of publication was observed, however in 2020, the significant increasing happened. The probable reason for this is progress in computer methods of simulation.

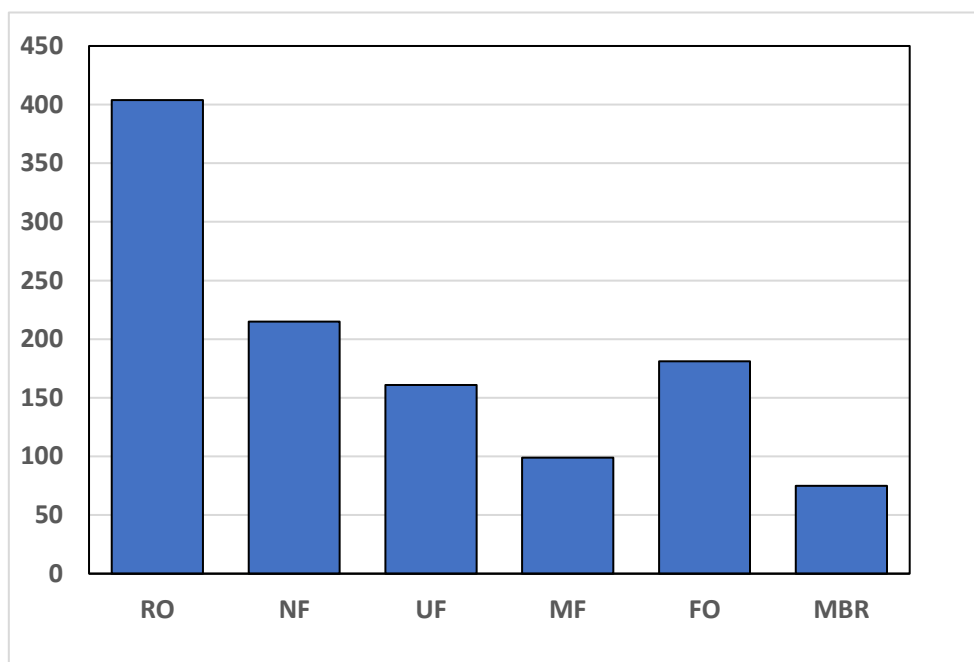


Fig. 1. The Number of publications dedicated to the simulation of each pressure-driven membrane process from 2011 to 2020 [1].

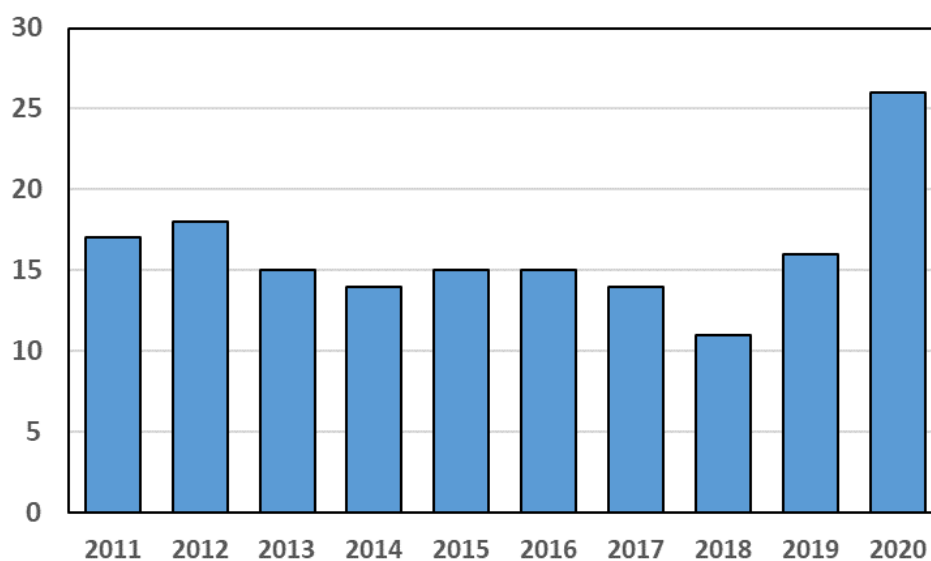


Fig. 2. The distribution of publications dedicated to the simulation of ultrafiltration over the years.

The distribution of the approaches to the simulation is shown in Fig. 3. Since, as in the previous period [1]. The application of the models based on irreversible thermodynamics and diffusion was limited. Therefore, these models were joined into one class. Also, the energy analysis was considered together with economic simulation in contrast with work [2] for the case of reverse osmosis.

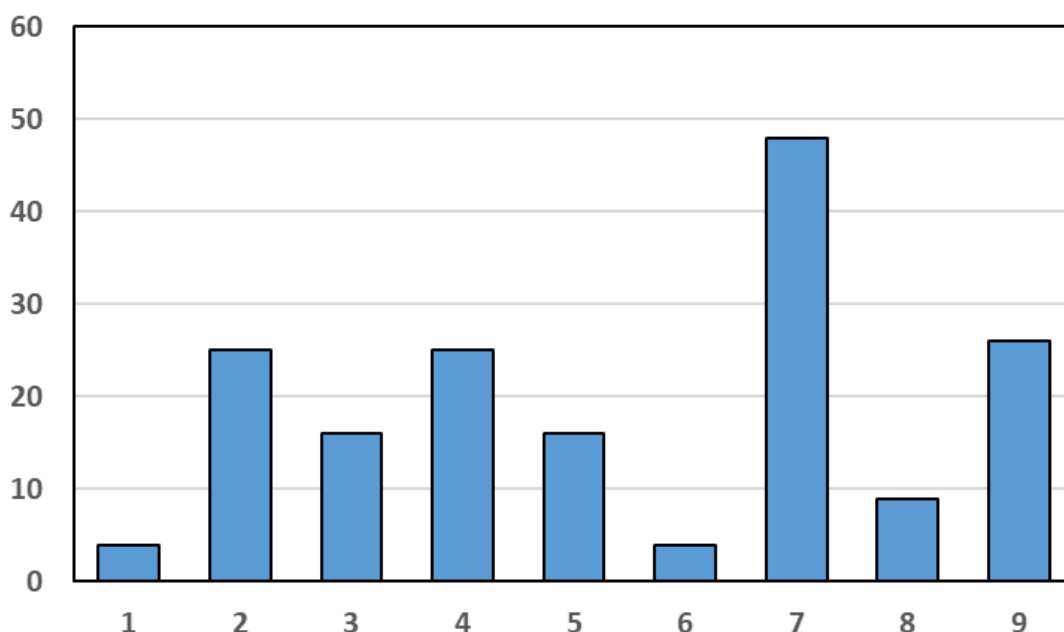


Fig.3. The number of UF models in the chosen articles by classes: 1 – irreversible thermodynamics and diffusion based models; 2 – pore models; 3 – resistance and concentration polarization based models; 4 – CFD models; 5 – ANN models; 6 – molecular dynamics; 7 – optimization; 8 – energy and economic analysis; 9 – other models.

Fig. 3 shows that the biggest number of publications is dedicated to the issues of the optimization of the UF process. Also, it draws attention to the significant number of articles, where the models using artificial neuron networks and concentration polarization were considered. However, the approaches based on the pore flow and computational fluid dynamics were applied the most often.

These results are in agreement with the generally accepted concepts about the structure of the ultrafiltration membranes, which are considered as porous. In such cases, the concepts of irreversible thermodynamics and diffusion are not effective simulation tools in contrast to the pore flow.

Considering the pore flow, the approaches with the application of the Hagen–Poiseuille equation, Darcy's law, and Kozeny–Carman equation were applied most often. However, in some works, the approaches using the extended Nerst–Plank equation and the Donnan equilibrium were considered. These concepts are more typical for the nanofiltration process [1, 3]. But the number of such works is relatively low, therefore, it is not reasonable to allocate them to a separate class.

Also, it is well known that ultrafiltration suffers from phenomena of concentration polarization and fouling to a greater extent in comparison with reverse osmosis and nanofiltration processes, which were considered in works [2, 3]. In this case, the significant number of theoretical investigations, where these phenomena are taken into account, seems to be logical. Also, for this reason, the application of the methods based on artificial neuron networks for the simulation of ultrafiltration is wider. In works [1], it was pointed out that these methods are especially effective when the physical picture of the process is complicated. It should be noticed that in some works

the models that take into account the resistances are based on artificial neuron networks [5] and also with other statistical methods [6].

The simulation of the pressure driven membrane processes with using of computational fluid dynamics and molecular dynamics is developing most dynamically [1-3]. This trend is also observed for ultrafiltration, as can be seen in Fig. 3. It should also be noticed that for the simulation of ultrafiltration, the same software is used as for other processes, in particular ANSYS Fluent [7], COMSOL [8], and NAMD [9].

Conclusions

The level of interest in the simulation of the UF process is still stable, and the significant changes in comparison with the previous period were not defined. Since then, the main conclusions and recommendations about choosing the most suitable strategy for the simulation of the UF process presented in work [1] are still relevant.

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Mathematical Modeling of Heat and Mass Transfer and Phase Transformations in the Condensation Zone of a Heat Pipe

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Abstract. *A mathematical model and numerical calculation method for the dynamics of heat and mass transfer in the condensation zone of a cylindrical heat pipe have been developed. The model describes the combined problem of condensation of working fluid vapor on a metal-fiber capillary-porous structure, diffusion-filtration transfer of heat and condensate through the wick, condensate removal to the transport zone, thermal conductivity in the pipe wall, and heat removal from the outer surface of the wall to the cooling coolant.*

Keywords: heat pipe, capillary structure, steam condensation, volumetric concentration of condensate, cooling intensity.

Introduction

Heat pipes are widely used for thermal stabilization of power equipment, electric motors, radio electronic devices, aircraft, and spacecraft, etc. This is due to the fact that, firstly, the heat transfer characteristics of heat pipes are several orders of magnitude higher than those of any highly thermally conductive material [1]. Secondly, the selection of effective geometric and operating characteristics for specific operating conditions ensures the removal of heat flows of any magnitude [2]. The creation of heat pipes and the identification of ways to control their operation is based on conducting detailed laboratory studies of heat and mass transfer and phase transformations depending on the selected geometry of the body, the nature of the working substance, the conditions of heat supply and removal, and some other factors. The use of mathematical modeling will allow for determining the optimal operating and structural characteristics of heat pipes at the design stage.

Results and discussion

The computational domain for which the problem was solved is shown in Fig. 1. It is slightly simplified for the end of the pipe. This allowed us to limit the use of only a cylindrical coordinate system for recording the mathematical model.

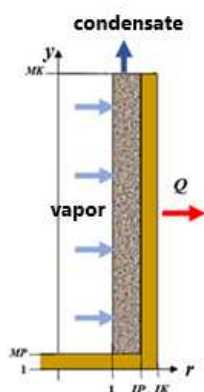


Fig. 1. View of the calculation area.

The steam condenses on the branched surface of the wick, filling the pores with a vapor-liquid mixture. At the same time, the concentration of the liquid in the wick increases, and the condensation heat is released. This process is continuous, since the formed liquid is discharged through the transport zone into the evaporation zone, where it begins to boil due to the heat of the surfaces that need to be thermally stabilized. Thus, the mathematical model includes differential transport equations of fluid, vapor, and energy

$$\frac{\partial U_{fl}}{\partial t} + \frac{\partial(w_{fl,r}U_{fl})}{\partial r} + \frac{\partial(w_{fl,y}U_{fl})}{\partial y} = \frac{1}{r} \frac{\partial}{\partial r} \left(D_{fl,r} \frac{\partial U_{fl}}{\partial r} \right) + \frac{\partial}{\partial y} \left(D_{fl,y} \frac{\partial U_{fl}}{\partial y} \right) + I_V, \quad (1)$$

$$\frac{\partial U_v}{\partial t} + \frac{\partial(w_{vr}U_v)}{\partial r} + \frac{\partial(w_{vy}U_v)}{\partial y} = \frac{1}{r} \frac{\partial}{\partial r} \left(D_v r \frac{\partial U_v}{\partial r} \right) + \frac{\partial}{\partial y} \left(D_v \frac{\partial U_v}{\partial y} \right) - I_V, \quad (2)$$

$$c_{ef} \left(\frac{\partial T}{\partial t} + w_{efr} \frac{\partial T}{\partial r} + w_{efy} \frac{\partial T}{\partial y} \right) = \frac{1}{r} \frac{\partial}{\partial r} \left(\lambda_{ef} r \frac{\partial T}{\partial r} \right) + \frac{\partial}{\partial y} \left(\lambda_{ef} \frac{\partial T}{\partial y} \right) + LI_V. \quad (3)$$

Heat transfer in the heat pipe's cylindrical wall is calculated using the Fourier equation

$$cp \frac{\partial T}{\partial t} = \frac{1}{r} \frac{\partial}{\partial r} \left(\lambda r \frac{\partial T}{\partial r} \right) + \frac{\partial}{\partial y} \left(\lambda \frac{\partial T}{\partial y} \right). \quad (4)$$

Here, T – temperature; U_{fl} and U_v – volume concentrations of liquid and steam; t – time; c_{ef} – effective specific volumetric heat capacity of a peat particle, $c_{ef} = c_b \rho_b \Psi_b + c_{fl} U_{fl} + c_v U_v$; c_b , c_{fl} , c_v – specific mass heat capacities of the solid phase, water and steam, ρ_b and Ψ_b – density and volume fraction of the solid phase, $\Psi_b = 1 - \Pi$, Π – porosity; λ_{ef} – effective thermal conductivity, $\lambda_{ef} = \lambda_b \Psi_b + \lambda_{fl} U_{fl} / \rho_{fl} + \lambda_v U_v / \rho_v$, ρ_v – density, $\psi = fl, v$; D_{fl} and D_v – diffusion coefficients of liquid and vapor phases; I_V – the intensity of phase transitions in the body pores; L – latent heat of phase transitions; w_{efr} – effective rate of filtration of the bound substance along the coordinate r , $w_{efr} = [w_{flr} c_{fl} U_{fl} + w_{vr} c_v U_v] / c_{ef}$, where w_{flr} , w_{vr} – filtration rates of liquid and vapor phases.

The diffusion coefficient of the liquid phase is determined by the formula of N.I. Nikitenko [3]: $D_{fl} = \gamma_{Dfl} [\exp(A_D / R_u T) - 1]^{-1}$, where R_u – universal gas constant, A_D – activation energy of diffusion transfer, γ_{Dfl} – diffusion coefficient. Diffusion coefficients for vapor phase components are found according to the well-known formula [4]: $D_v = \gamma_{Dv} T^{3/2} / P_v$, where P_v – vapor phase pressure, γ_{Dv} – diffusion coefficient.

The filtration rates of the liquid w_{fl} and vapor w_v phases are proportional to the pressure gradients of the corresponding phase and can be calculated by Darcy's formula $w_\psi = -K \nabla P_\psi / \mu_\psi$, where $\psi = fl, v$; K – permeability of the metal-fiber medium, $K = 0,4 d_{fib}^{2,75} \exp(8,4 \cdot 10^{-3} \Pi d_{fib}^{-0,22})$ [5], d_{fib} – diameter of the fibers forming the capillary-porous structure in microns.

The partial pressures P_{fl} and P_v are calculated through functions U_{fl} , U_v , and T . Pressures of the vapor phase are found using the equation of state for diluted gases $P_v = \rho_v R_u T / \mu_v$, here the partial densities of steam $\rho_v = U_v / \Psi_v$, volume fraction of the vapor and phases $\Psi_v = \Pi - \Psi_{fl}$, and $\Psi_{fl} = U_{fl} / \rho_{fl}$. Liquid phase pressure will be $P_{fl} = P_v + P_{cap}$, where the capillary pressure P_{cap} is calculated [4] as the average capillary pressure of the liquid. The volume of liquid $dV(r)$, contained in capillaries with a radius from r to $r + dr$ in a unit volume of the body is proportional to the differential function $f(r)$ of the capillary size distribution and the volume fraction $\theta(r)$ of the capillary, which is occupied by liquid: $dV(r) = \theta(r) f(r) dr$. Then the average value of the capillary pressure at a given point of the body is represented by an expression similar to the Laplace equation

$$P_{cap} = 2\sigma(T) \int_{r_{min}}^{r_{max}} \frac{\theta(r)}{r} f(r) dr / \int_{r_{min}}^{r_{max}} \theta(r) f(r) dr = \frac{2\sigma(T)}{r^*}, \quad r_{min} < r^* < r_{max}, \quad (5)$$

where r_{min} , r_{max} – minimum and maximum pores radius; r^* – characteristic parameter of pore size dispersion.

The function $\theta(r, t)$ in a capillary of radius r at time t is determined by the expression obtained as the ratio of the cross-sectional area of the capillary occupied by liquid to its total cross-sectional area $\theta(r, t) = \pi[r^2 - (r - \delta)^2] / \pi r^2 = 1 - (1 - \delta/r)^2$, where δ is the thickness of the liquid

layer on the walls of partially filled capillaries, $\delta = \delta^* \bar{\delta} = \delta^* (1 - \sqrt{1 - \varphi})$ [6], δ^* – the average displacement length of an activated particle in the liquid layer, $\varphi = P_v / P_s(T)$, $\bar{\delta} = \delta / \delta^*$ when $0 < \delta < \delta^*$ and $\bar{\delta} = 1$ when $\delta > \delta^*$. The value δ^* can be considered as the thickness of the boundary layer. It is adjacent to the free surface of a rather massive condensed body in which the evaporation process takes place. The saturation pressure was calculated according to the formula of N.I. Nikitenko [6]: $P_s = N_p \sqrt{T} [\exp(A / R_u T) - 1]^{-1}$, $N_p = 0,4361 \cdot 10^{10} \text{ kg/(m} \cdot \text{s}^2 \cdot \text{K}^{0.5})$, $A = 0,4206 \cdot 10^{-15} \text{ J}$. The values of A and N_p were found as a result of the solution of the system of two equations obtained by writing this equation for two points on the saturation line. They correspond to the values of T_1, P_{s1} and T_2, P_{s2} in the table of saturated steam and water, respectively. Formula for P_s is valid for liquids of various natures, and is quite accurate.

The phase transformations intensity is found as the difference between the flows of evaporating liquid and condensing vapor. For the contact surface of vapor coming from the heating zone with temperature T_v and humidity φ_v and the wick, the formula [6] has the following form

$$I = \gamma_{fl-v} \left\{ \varphi_b \left[\exp(A / RT|_{v=0}) - 1 \right]^{-1} - \varphi_v \left[\exp(A / RT_v) - 1 \right]^{-1} \right\}, \quad \gamma_{fl-v} = \varepsilon \rho_{fl} \delta^* / 4. \quad (6)$$

Here ε – radiation coefficient; v – normal to the boundary surface; A – activation energy. The multiplier $\varphi_b = \bar{\delta}(2 - \bar{\delta})$ represents the relative humidity of the gas-vapor mixture, to which, according to the sorption isotherm, the volume concentration U_{fl} at a given point on the surface corresponds. The condensation intensity in the capillaries of the wick is found by the formula that follows from (6) under the condition of local thermodynamic equilibrium, according to which the temperatures of the phases at the point of their contact are the same:

$$I_v = \gamma_{fl-v} \left[\exp(A / RT) - 1 \right]^{-1} (\varphi_b - \varphi_v) S, \quad (7)$$

where S is the contact area of the liquid and gas phases in the wick pores that are not completely filled with liquid $S = \frac{2\sqrt{1-\varphi_b}}{\rho_{fl}\delta^*} \frac{\partial U_{fl}}{\partial \varphi_b}$, derivative $\partial U_{fl} / \partial \varphi_b$ is determined by differentiating the desorption isotherm equation.

The boundary conditions for the computational domain (Fig. 1) are formulated as follows. On the surface $r=1$, $MP \leq y \leq MK$ boundary conditions of the third kind occur:

$$D_{fl} \frac{\partial U_{fl}}{\partial r} \Big|_{r=1} + \frac{\partial(w_{flr} U_{fl})}{\partial r} \Big|_{r=1} = I|_{r=1}; \quad -D_v \frac{\partial U_v}{\partial r} \Big|_{v=0} + \frac{\partial(w_{vr} U_v)}{\partial r} \Big|_{v=0} = -\gamma_{v,ei} (U_v|_{r=1} - \rho_{v,ei} \Psi_v),$$

$$\lambda_{ef} \frac{\partial T}{\partial r} \Big|_{r=1} + w_{efr} \frac{\partial T}{\partial r} \Big|_{r=1} = \alpha(T_{ei} - T|_{r=1}) + L I|_{r=1}. \quad (8)$$

On the borders $r = IP$, $MP \leq y \leq MK$ and $y = MP$, $1 \leq r \leq IP$ only heat transfer occurs. For the surface $r = IP$, $MP \leq y \leq MK$ the boundary conditions have the following form:

$$\lambda \frac{\partial T}{\partial r} \Big|_{r=IP} = \lambda_{ef} \frac{\partial T}{\partial r} \Big|_{r=IP} + w_{efr} \frac{\partial T}{\partial r} \Big|_{r=IP}; \quad \frac{\partial U_{fl}}{\partial r} \Big|_{r=IP} = 0; \quad \frac{\partial U_v}{\partial r} \Big|_{r=IP} = 0. \quad (9)$$

Through the boundary $1 \leq r \leq IP$, $y = MK$, the condensate is continuously removed under the action of capillary forces into the transport zone, and the change in temperature and volumetric

vapor concentration at this boundary can be neglected. Then the boundary conditions are written in the following way:

$$\left. \frac{\partial T}{\partial y} \right|_{y=MK} = 0; \quad -D_{fl} \left. \frac{\partial U_{fl}}{\partial y} \right|_{y=MK} + \left. \frac{\partial (w_{fl} U_{fl})}{\partial y} \right|_{y=MK} = \frac{K}{\mu_{fl}} \frac{P|_{y=MK} - P_{cap}}{\partial y} U_{fl}|_{y=MK}; \quad \left. \frac{\partial U_v}{\partial y} \right|_{y=MK} = 0; \quad \left. \frac{\partial w_{vx}}{\partial x} \right|_{x=0} = 0;$$

$$\left. \frac{\partial w_{fly}}{\partial y} \right|_{y=MK} = \frac{K}{\mu_{fl}} \frac{P|_{y=MK} - P_{cap}}{\partial y}. \quad (10)$$

Heat removal from the outer wall of a heat pipe is carried out by free or forced convection.

The implementation of the presented mathematical model, the equations of which contain convective terms, was carried out by a numerical method based on the three-layer explicit recalculated difference scheme of Nikitenko M.I. [4].

Figs. 2, 3 present the calculation results. A copper heat pipe was considered. The length of the condensation zone was taken as 0.25 m, the wall thickness was 0.004 m, the wick thickness was 0.012 m, the diameter of the fibers of the metal fiber structure was $d_v = 20 \mu\text{m}$ and its porosity $\Pi = 0.7$. The following initial physical parameters were taken as: $T_0 = 283 \text{ K}$; $U_{fl0} = 6,98 \text{ kg/m}^3$; $P_{v0} = 1,187 \text{ kPa}$; $P_{s0} = 1,199 \text{ kPa}$; $T = 353 \text{ K}$; $T_{e,i} = 283 \text{ K}$; $P = 47 \text{ kPa}$; $P_v = 46.79 \text{ kPa}$; $A = A_D = 0.4205 \cdot 10^8 \text{ J/kmol}$; $\lambda_b = 395 \text{ W/(m}\cdot\text{K)}$; $c_b = 385 \text{ J/(kg}\cdot\text{K)}$; $\rho_b = 8890 \text{ kg/m}^3$. Sorption isotherm equation for a porous copper structure [7]: $W^{-1} = W_{\max}^{-1} - 35,5 \ln \varphi$, where the maximum moisture content $W_{\max}$ corresponds to the value $\varphi = 1$ and $T = 20^\circ\text{C}$ is equal to 0.45%, and $U_{fl} = 0,01 W \rho_T$.

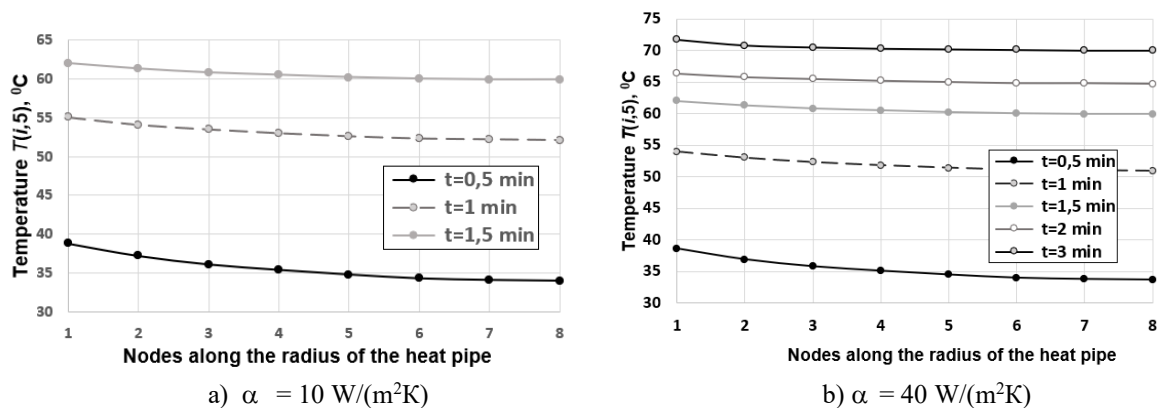


Fig. 2 Temperature change at some points in time along the Or axis in the wick ($i=1, \dots, 6$) and the wall ($i=6, 7, 8$) of the heat pipe at the nodal point along the coordinate $Oy \ m=MP+2$ (Fig. 1) at different intensities of heat transfer from the outer wall.

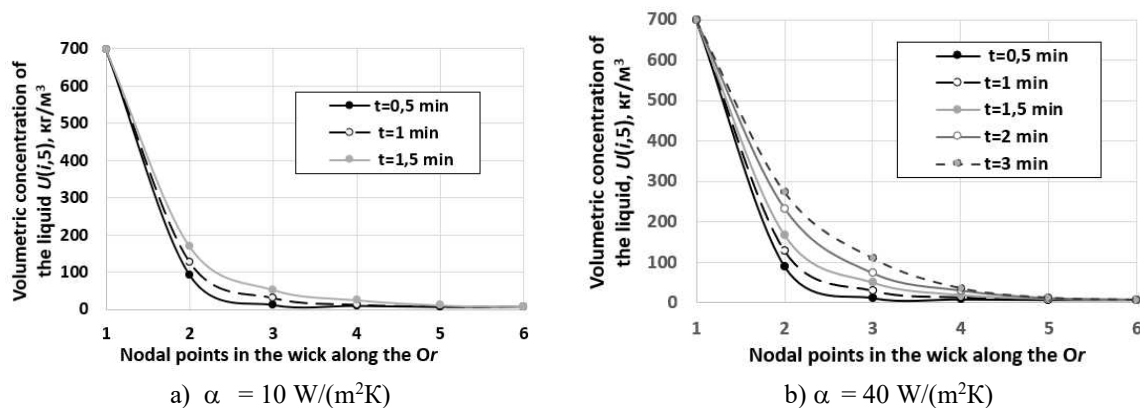


Fig. 3 Change of U_{fl} in a porous wick ($i=1, \dots, 6$) at some moments of time along the Or axis at the nodal point along the coordinate $Oy \ m=MP+2$ (Fig.1) at different intensities of heat transfer from the outer wall.

Conclusions

The developed mathematical model and the method of its implementation show adequate qualitative results and can be useful in analyzing various influencing factors on the efficiency of the heat pipe when designing or selecting operating modes.

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Topological Optimization of Mass Characteristics of a Lower Limb Prosthesis Stump Receiver Using SolidWorks

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Abstract. Topological optimization of the 3D model of the stump receiver of the lower limb prosthesis was carried out in order to reduce its mass. The resulting model is suitable for the manufacture of a functional stump receiver of the prosthesis using additive manufacturing methods and is characterized by a reduced mass while maintaining the initial strength of the structure.

Keywords: prosthesis, topological optimization, mass, 3D model, SolidWorks.

Introduction

Topological optimization is an advanced engineering design method that allows you to find the most efficient shape or structure of an object, taking into account given constraints such as loads, materials, geometry, and mass characteristics. It is actively used in the automotive industry, aviation and astronautics, construction, and mechanical engineering. Topological optimization can also be used in medicine, in particular for the development of prostheses, implants, and other medical devices. Such an implementation of topological optimization allows you to create lightweight and comfortable structures that meet the anatomical requirements of patients and produce more ergonomic and effective prosthetic and orthopedic products, and improve prosthetic designs.

Lower limb prostheses are important technical devices that provide mobility and comfort to patients who have lost one or more limbs. Their manufacture requires consideration of numerous factors, including comfort, reliability, durability, and, importantly, optimization of mass characteristics. Since the mass of a prosthesis has a great influence on the comfort and efficiency of its use, proper material distribution allows for weight reduction without reducing the strength and functionality of the prosthesis.

Thus, the main task of topological optimization in the design of lower limb prostheses can be considered to be reducing their mass. By minimizing the amount of material used in different parts of the prosthesis, it is possible to achieve a significant reduction in its total mass while maintaining the necessary structural strength. This is important for the convenience of wearing the prosthesis, reducing the load on other parts of the body, which contributes to a longer and more effective use of the prosthesis. Topological optimization allows you to distribute the material in

places where it is needed to withstand maximum loads, thus increasing the durability of the prosthesis and reducing the risk of its damage or breakage.

Prosthetic designs obtained using topological optimization are, as a rule, practically impossible to manufacture using classical prosthetic technologies. Additive technologies are optimal for such designs. Additive technologies also allow the use of new materials (aluminum and titanium alloys, engineering plastics (polycarbonate, polyamide)) in the designs of prosthetic stump receivers and the most effective use of their properties.

From the perspective of taking into account the individual needs of the patient, topological optimization can help create prostheses that are most suitable for the specific physical characteristics of the user, taking into account their weight, size, and motor characteristics, which is not always possible in classical technologies.

In general, the application of topological optimization methods in the creation of lower limb prostheses is promising and will significantly improve the quality of life of patients, as well as generally unify the entire process of manufacturing prostheses using additive technologies. At the same time, it opens up new opportunities for personalization and individualization of prostheses, which can provide a higher level of functionality and comfort for users.

Experimental

The object of study of this work was the stump receiver of the lower limb prosthesis. The main goal of the work was to establish the possibility of optimizing the mass characteristics of the stump receiver of the prosthesis while maintaining all the functional and strength properties of the original model. The original model of the stump receiver was created as a result of scanning the patient's stump and processing the resulting scan to obtain a 3D model containing all the necessary functional elements (Fig. 1).

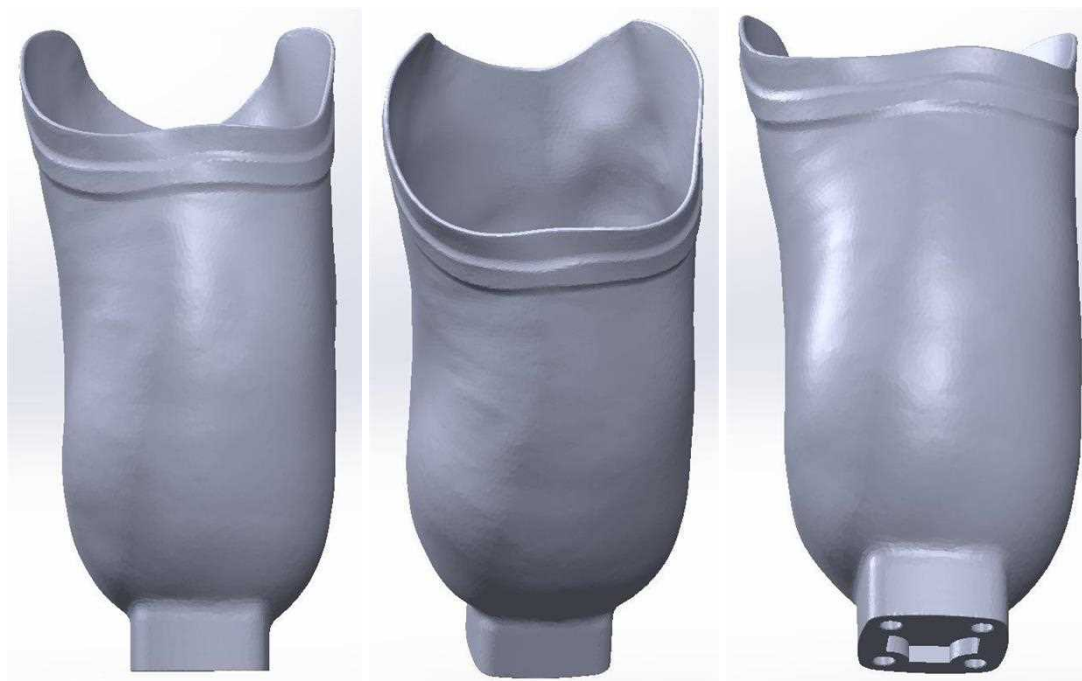


Fig. 1. Initial 3D model of the lower limb prosthesis stump receiver.

The material chosen for the manufacture of the stump receiver was Nylon 6/10 ($\rho=1.4 \text{ g/cm}^3$). While the initial mass is 430.27 g. The wall thickness is from 2 to 5 mm, the thickness of the element intended for fastening the sleeve adapter is 27 mm (Fig. 2).

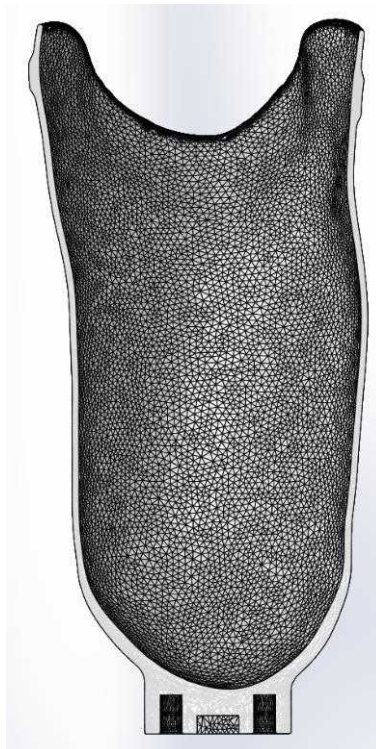


Fig. 2. Section of the model of the stump receiver of the lower limb prosthesis.

Topological optimization of the stump receiver was performed using parametric and modeling functions of the SolidWorks program. The goal of topological optimization was to reduce the mass of the stump receiver while maintaining its mechanical properties, which will also reduce material consumption during manufacturing.

The first step in the optimization was to establish the loading conditions and constraints for the initial 3D model, which included fixing the points and the loads acting on the model. The load was selected based on the weight of the patient for whom this prosthesis is intended (750 N), and the attachment point was the lower functional element, which is intended for attaching the sleeve adapter with a flat platform. The goal of the study was to obtain the best strength-to-weight ratio.

Two types of simulations were performed, which differed in the initial conditions regarding the inner surface of the stump receiver. In the first case, the inner surface was not considered as a preserved (frozen) area, in the second, the inner surface was preserved with a depth of 1 mm. This approach allowed us to obtain different variants of the optimized stump receiver design. In the first case, the optimized design involves obtaining a stump receiver with through holes, and in the second, with the preservation of a continuous inner shell.

The results of topological optimization of the stump receiver without preserving the inner surface are shown in Figure 3. Here, the volume of material that can be removed without losing the rigidity of the stump receiver design is shown in blue. The mass of the stump receiver with complete removal of material, in this case, reaches only 53% of the initial mass and is 228.04 grams. The resulting stump receiver design with through holes, although it is characterized by a significantly lower mass, cannot be used for fixation on the patient's stump using a vacuum fixation system. In this case, it is necessary to consider other fixation systems, in particular liners with a locking system.

To be able to use a vacuum attachment system, it is necessary to provide a thin layer of material on the inner surface of the stump receiver. This design is a compromise but can also be considered fully functional and usable.

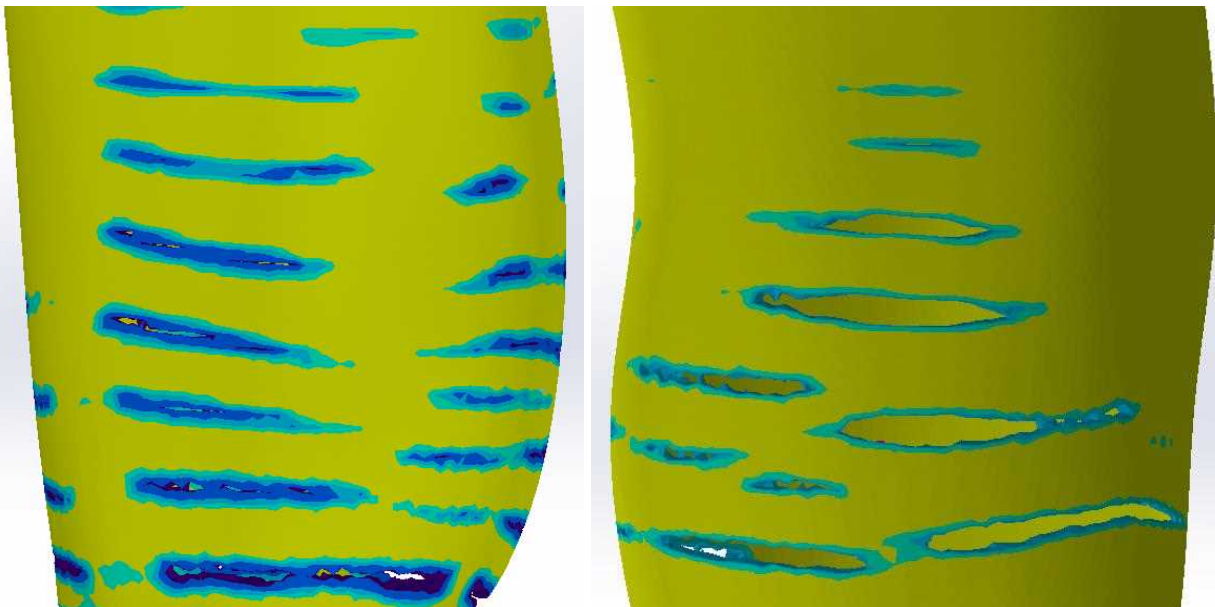


Fig. 3. Results of topological optimization without preserved regions.

If in the previous case the material from the model was removed from small local areas, then in this case the surface area of the stump receiver from which it is proposed to remove material is much larger (Fig. 4). At the same time, the maximum mass reduction reaches only 64% of the initial one (275.4 g).

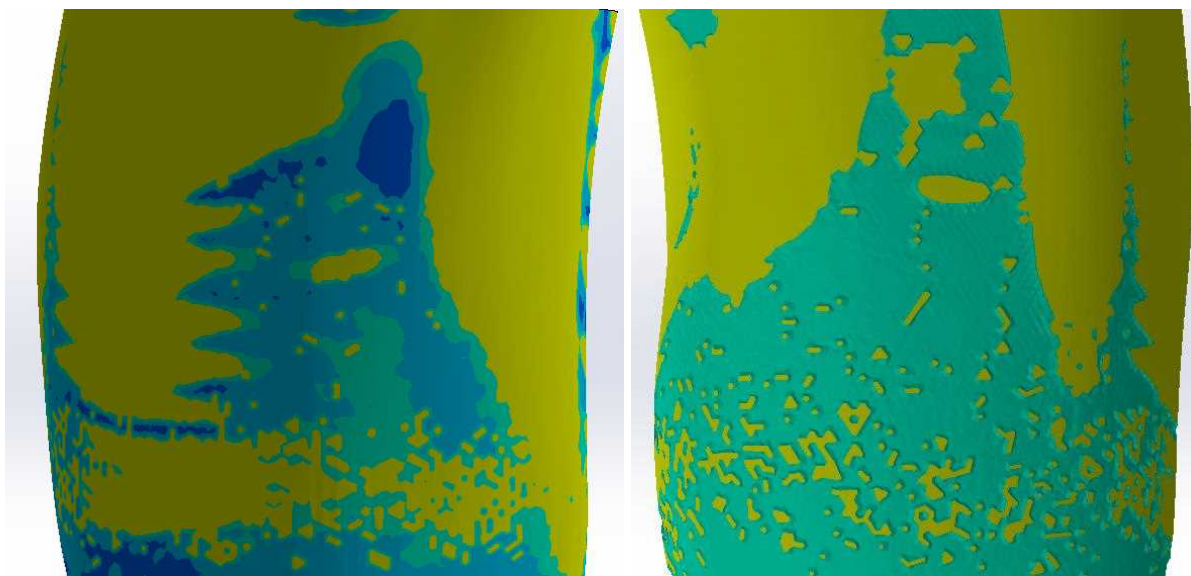


Fig. 4. Results of topological optimization with preservation (freezing) of the inner surface.

It should be noted that the resulting optimized designs of stump receivers cannot be obtained within the framework of traditional prosthetic technologies (especially in the case of preserving the inner surface layer). Such complex designs require the use of additive technologies, 3D scanning, and the widespread implementation of automated design systems.

Conclusions

Thus, the results of the topological optimization of the mass characteristics of the stump receiver of the lower limb prosthesis showed that it is possible to achieve a significant reduction in the mass of the stump receiver and, as a result, the prosthesis as a whole. The use of modern 3D technologies is promising and has significant prospects in prosthetics.

AI-Driven Predictive Modeling for Biomass Carbon Sequestration and Decarbonization

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Abstract. As climate change mitigation gains urgency, AI-driven predictive modeling optimizes biomass-based carbon sequestration, enhancing efficiency and supporting decarbonization. This article explores machine learning techniques, data sources, and real-world applications that improve carbon capture, contributing to sustainable environmental management and global CO₂ reduction efforts.

Keywords: AI-driven carbon sequestration, predictive modeling, decarbonization, biomass, AI in climate mitigation, carbon capture optimization.

Introduction

Decarbonization requires innovative solutions to reduce greenhouse gas (GHG) emissions and enhance carbon sinks. Biomass, including forests, agricultural crops, and bioenergy plantations, plays a critical role in capturing and storing carbon through photosynthesis. However, accurate prediction of carbon sequestration potential is complex, as it depends on various factors such as climate, soil properties, plant physiology, and land management practices. AI-driven predictive modeling presents a promising approach to overcome these challenges, enabling more precise assessments and optimization of biomass carbon sequestration. Recent studies have demonstrated the effectiveness of AI models in mapping and forecasting biomass carbon storage, particularly in forested regions where sequestration rates vary based on tree species, age, and environmental conditions. For instance, neural networks have been applied to estimate carbon uptake in boreal forests by analyzing satellite imagery and climate datasets, showing a high correlation with field measurements [1].

AI Techniques in Predictive Modeling for Biomass Carbon Sequestration

Artificial intelligence has revolutionized predictive modeling by leveraging complex algorithms capable of analyzing vast amounts of ecological data. Machine learning techniques, such as artificial neural networks and decision trees, have been widely implemented in predicting biomass carbon sequestration. One notable application involves using deep learning models to assess carbon storage potential in urban green spaces, where factors such as species diversity and land use changes significantly influence sequestration rates. A case study conducted in urban environments demonstrated that AI-enhanced predictive models could outperform traditional statistical methods by incorporating real-time data from IoT sensors and satellite observations [2].

A simple AI-driven model can use input parameters such as biomass type, growth rate, soil carbon content, and climatic conditions to predict the potential carbon sequestration capacity of different biomass sources. The table below (Table 1) presents an example of input data and predicted carbon sequestration potential for various biomass types. This predictive modeling example illustrates how AI can efficiently process multiple ecological variables to forecast sequestration outcomes. By refining these models with real-time data, AI can enhance the accuracy of carbon offset planning, assist policymakers in land management decisions, and optimize biomass selection for sustainable decarbonization efforts.

Table 1

AI-Based Prediction of Biomass Carbon Sequestration

Biomass Type	Growth Rate (kg/year)	Soil Carbon Content (%)	Climatic Condition	Predicted Sequestration (kg CO ₂ /year)
Salix (Willow)	30	2.5	Temperate	85
Miscanthus	50	3.0	Humid	120
Pine Forest	80	4.2	Cold	200
Algae Farm	100	N/A	Marine	250

Another promising application of AI-driven predictive modeling is in precision agriculture. By integrating AI with remote sensing technologies, researchers have successfully developed models that optimize bioenergy crop selection based on soil carbon retention capacity and climate variability. In a recent study, AI-assisted analysis of soil health and crop growth patterns led to a 20% increase in sequestration efficiency when compared to conventional agricultural practices [3]. Moreover, reinforcement learning techniques have been applied to forest management strategies, enabling dynamic adjustments to afforestation and deforestation policies based on projected carbon storage outcomes.

AI Applications in Biomass-Based Decarbonization Strategies

AI-based predictive models have been employed in a variety of settings to improve biomass carbon sequestration, revolutionizing the way scientists and policymakers optimize land use and resource allocation. One of the most significant applications is in large-scale afforestation projects, where machine learning algorithms have played a crucial role in selecting optimal tree species and planting locations. These models assess historical climate data, soil characteristics, and carbon sequestration rates of various species to recommend the most effective reforestation strategies. AI-based predictive modeling is especially useful in reforestation efforts in climate-sensitive regions, where environmental conditions fluctuate, requiring adaptable planting techniques[4].

For example, AI-assisted models have been used to evaluate the effectiveness of mangrove reforestation efforts, identifying regions where carbon sequestration rates are maximized due to tidal influences and soil composition. These models help conservationists determine which coastal areas provide the highest potential for long-term carbon storage while protecting against soil erosion and storm surges. By continuously analyzing remote sensing data, AI can also track mangrove health, predicting degradation risks and offering proactive intervention strategies. This allows policymakers to make data-driven decisions regarding afforestation investments and land use planning, ensuring a more sustainable approach to ecosystem restoration.

Beyond reforestation, AI-driven predictive modeling has also been applied in the bioenergy sector, particularly in optimizing the lifecycle analysis of energy crops such as Miscanthus and switchgrass. These crops are increasingly used for biofuel production and have been recognized for their potential to absorb CO₂ while providing a renewable energy source. By analyzing historical data on growth rates, soil nutrient content, water availability, and carbon absorption rates, AI models can recommend planting schedules, fertilization techniques, and irrigation strategies that maximize sequestration while maintaining economic viability [5].

Moreover, AI-based simulations allow farmers and bioenergy producers to predict long-term sequestration efficiency, ensuring that the cultivation of bioenergy crops does not lead to soil degradation or reduced productivity. Research suggests that AI-driven optimization of crop rotation cycles can increase soil carbon retention while preventing nutrient depletion, making it a vital tool for sustainable agriculture. This has significant implications for carbon credit markets, as AI-generated sequestration data provides a transparent and verifiable assessment of carbon offset projects, helping bioenergy producers participate in carbon trading programs more effectively.

In addition to land-based applications, AI has been increasingly utilized in ocean-based carbon sequestration strategies. The role of phytoplankton in the global carbon cycle has been well-documented, with these microorganisms responsible for capturing large amounts of atmospheric CO₂ and transporting it to deep ocean layers. However, accurately modeling phytoplankton bloom patterns and their carbon sequestration potential has been a longstanding challenge due to oceanic variability and limited observational data.

Recent research has focused on developing AI-driven predictive models that analyze satellite and oceanographic data to improve sequestration estimates. AI algorithms trained on real-time ocean temperature, nutrient levels, and chlorophyll concentrations can detect the onset of phytoplankton blooms and predict their carbon sequestration efficiency. These models enable scientists to understand how climate change is affecting marine carbon sinks, allowing them to devise targeted interventions such as controlled iron fertilization, which enhances phytoplankton growth and increases CO₂ absorption.[6]

Furthermore, AI is now being integrated with autonomous underwater drones to monitor deep-sea carbon sequestration in seagrass meadows, kelp forests, and blue carbon ecosystems. These AI-powered drones collect and analyze real-time data on carbon storage rates, helping researchers gain a more comprehensive understanding of oceanic carbon fluxes. This not only improves global climate models but also supports policy development for marine conservation and carbon credit systems.

As AI-based predictive models continue to evolve, their applications in carbon sequestration will expand beyond their current capabilities. Future advancements may include AI-assisted genetic analysis of high-sequestration plant species, real-time soil carbon measurement using smart sensors, and AI-driven optimization of hybrid reforestation and agricultural systems. By combining AI with emerging technologies such as blockchain for carbon tracking and IoT for environmental monitoring, researchers and policymakers can significantly enhance the efficiency and transparency of carbon sequestration initiatives, making AI an indispensable tool in the fight against climate change.

AI and Remote Sensing for Enhanced Carbon Sequestration Monitoring

The integration of artificial intelligence (AI) with remote sensing technologies has significantly improved the ability to monitor and predict biomass carbon sequestration. Remote sensing, facilitated by satellite imagery, LiDAR, and drone-based monitoring, provides continuous and large-scale environmental data that can be analyzed using AI-driven algorithms. These technologies allow researchers to track vegetation changes, assess biomass growth, and estimate carbon sequestration rates with high accuracy.

Machine learning models trained on multispectral and hyperspectral satellite data have been used to detect variations in forest density, plant health, and carbon sequestration efficiency across different ecosystems. AI-based tools, such as convolutional neural networks (CNNs), can process

these high-resolution images to classify land cover changes and predict carbon storage potential in real time. For instance, Sentinel-2 and Landsat imagery, when combined with AI models, have been used to estimate forest carbon stocks with an accuracy exceeding 85%.

Furthermore, AI-powered remote sensing enables rapid detection of deforestation, wildfires, and land-use changes that impact carbon sequestration. By incorporating near-real-time updates, AI systems can assist policymakers in making timely decisions to mitigate carbon losses due to human activity or natural disturbances. The combination of AI and remote sensing not only enhances monitoring accuracy but also reduces the cost and time associated with traditional field-based carbon measurement methods.

As AI-driven remote sensing continues to advance, it will play an increasingly crucial role in refining carbon sequestration models, enabling adaptive land management strategies, and ensuring more effective climate mitigation policies.

Economic Advantages of Using AI for Decarbonization

The integration of artificial intelligence (AI) in decarbonization efforts provides significant economic benefits, making sustainable environmental practices more cost-effective and accessible. One of the primary economic advantages is the optimization of resource allocation, where AI-driven models can analyze vast datasets to recommend the most efficient strategies for carbon sequestration. By reducing reliance on traditional trial-and-error methods, AI helps businesses and governments minimize waste and improve return on investment in green initiatives. Another major advantage is cost reduction in carbon monitoring and reporting. Traditional carbon accounting methods require extensive manual data collection and analysis, often leading to inaccuracies and delays. AI automates this process by leveraging remote sensing, IoT devices, and big data analytics to provide real-time insights into carbon emissions and sequestration rates. This reduces operational costs for industries subject to carbon regulations and allows companies to optimize their participation in carbon markets.

Furthermore, AI enhances decision-making in carbon credit trading. AI-powered predictive models can forecast market trends, assess risk factors, and optimize trading strategies for carbon credits. This improves liquidity in carbon markets and helps businesses monetize their sequestration efforts more effectively. Additionally, blockchain integration with AI ensures transparency and trust in carbon offset transactions, reducing fraud and increasing investor confidence. The adoption of AI in bioenergy and reforestation projects also results in long-term economic benefits. AI-driven models help identify the most profitable bioenergy crops based on climate and soil conditions, ensuring high yields and sustainable land use. Moreover, by optimizing reforestation efforts, AI helps governments and organizations maximize the economic value of carbon sequestration projects through international carbon offset programs and sustainability grants. Industries transitioning to low-carbon supply chains benefit from AI-driven optimization in logistics and production. AI-powered systems improve energy efficiency in manufacturing and transportation, reducing overall carbon footprints while lowering costs. Smart grid management using AI allows businesses to integrate renewable energy sources more efficiently, reducing dependency on fossil fuels and benefiting from cost savings through demand-response mechanisms.

Overall, the use of AI in decarbonization offers compelling economic advantages by improving efficiency, reducing costs, and enhancing market participation. As AI continues to evolve, its applications in economic sustainability will become increasingly vital in driving global efforts towards carbon neutrality.

Challenges, Ethical Considerations, and Future Prospects of AI-Driven Carbon Sequestration

The integration of artificial intelligence (AI) in biomass carbon sequestration offers remarkable opportunities but also presents several challenges and ethical considerations that must be addressed to ensure responsible and effective implementation. One of the fundamental concerns is data accuracy and representativeness in AI models. Many sequestration predictions rely on historical datasets that may not fully capture the complexities of different ecosystems, leading to biased predictions. Inaccurate or incomplete data can result in ineffective sequestration strategies, affecting climate mitigation efforts.

Another significant challenge is the computational demand of AI models. Deep learning algorithms, particularly large-scale neural networks, require substantial processing power, which contributes to energy consumption and carbon emissions. As AI continues to be a major tool in carbon sequestration, researchers must focus on developing energy-efficient models and adopting cloud computing solutions powered by renewable energy to align AI use with sustainability goals.

AI-driven carbon sequestration models also raise concerns about transparency and accountability, particularly in carbon markets and policy frameworks. While AI can enhance accuracy in carbon offset estimations, an over-reliance on algorithmic predictions without proper validation poses risks. Establishing standardized methodologies for verifying AI-generated sequestration estimates is crucial to preventing their misuse in carbon credit trading and policy decision-making. Blockchain-based tracking systems integrated with AI could provide transparency and trust in carbon offset transactions.

Additionally, the use of AI in land management and reforestation efforts must consider ethical implications. AI-assisted decision-making in afforestation projects, if implemented without consulting local communities, may lead to displacement, biodiversity loss, and ecosystem imbalances. Ethical AI applications should prioritize sustainable land-use practices and community engagement to ensure that environmental conservation efforts benefit both the ecosystem and local populations.

Apart from ethical considerations, AI models face technical and scalability challenges. While AI-driven predictive models have demonstrated success in regional studies, their large-scale implementation requires robust computing infrastructure capable of processing vast datasets from diverse ecological settings. Issues such as inconsistencies in satellite imagery resolution, sensor calibration errors, and climate modeling uncertainties further complicate the widespread deployment of AI in biomass carbon sequestration.

Despite these challenges, the future prospects of AI in carbon sequestration remain promising. Advances in remote sensing technologies, deep learning, and quantum computing are expected to enhance the precision and efficiency of sequestration models. AI-powered real-time monitoring systems can significantly improve carbon stock estimations, enabling adaptive carbon sequestration strategies. Furthermore, integrating AI with emerging technologies such as blockchain-based carbon tracking and IoT-driven sensor networks will improve accountability and reliability in carbon markets.

For AI-driven carbon sequestration to be truly effective, a collaborative approach among AI researchers, ecologists, policymakers, and industry leaders is essential. Future developments should focus on increasing AI model transparency, minimizing computational footprints, and ensuring ethical AI deployment. With these advancements, AI has the potential to play a pivotal role in accelerating global decarbonization efforts and achieving long-term climate resilience.

Conclusions

AI-driven predictive modeling represents a transformative approach to improving carbon sequestration in biomass, offering a powerful tool for decarbonization strategies. By leveraging machine learning, remote sensing, and big data analytics, researchers and policymakers can enhance sequestration efficiency, support climate change mitigation efforts, and create sustainable carbon management frameworks. Continued advancements in AI will be crucial for unlocking the full potential of biomass as a key component of global decarbonization initiatives.

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Molecular Dynamics Modeling as an Innovative Approach to Solving Problems in Ecology

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Abstract. *Molecular dynamics modeling is a modern tool for analyzing and predicting molecular processes that is becoming increasingly relevant in addressing environmental challenges. This approach allows for an in-depth investigation into the mechanisms of pollutant formation at the atomic level, thereby aiding in the development of effective environmental protection strategies.*

Keywords: Molecular dynamics modeling, force fields, LAMMPS, Material Studio, polymer materials, ecology, interaction potentials.

Introduction

Molecular dynamics (MD) modeling is a modern tool for analyzing and predicting the behavior of molecules in various environments, which is becoming particularly relevant in addressing environmental issues. This approach enables a detailed study of chemical interactions at the atomic level, revealing the mechanisms of formation, dispersion, and transformation of materials that are harmful to the environment. Thanks to high-performance computing systems, MD modeling provides the opportunity to create accurate models that account for the physicochemical properties of environmental components, which is essential for developing effective strategies to combat environmental threats.

Building polyethylene molecules using Materials Studio

The innovative aspect of this approach lies in its ability to integrate theoretical knowledge with experimental data, allowing not only the prediction of environmental processes but also the optimization of methods for controlling them. For example, modeling the interactions of polymer waste during pyrolysis helps reveal the mechanisms behind the formation of both beneficial and potentially harmful products, ultimately leading to optimal solutions. Numerical models can identify the critical stages of the process where chemical bonds break, thereby enabling the adjustment of pyrolysis parameters (such as temperature, pressure, reaction duration, and catalyst use) to maximize the yield of desired products while minimizing the formation of toxic compounds. The data obtained contributes to the development of more efficient and environmentally safe technologies for processing polymer waste, allowing for preliminary assessments of the energy efficiency of the process and the economic feasibility of new disposal methods. Furthermore, a detailed analysis of molecular processes enables the adaptation of technologies to changes in the composition of raw materials, which is an important factor when working with various types of waste. Thus, MD modeling becomes a powerful tool for studying environmental processes, opening up new prospects for addressing pressing issues in environmental protection and the sustainable development of conservation technologies.

As an example of using MD modeling to analyze the pyrolysis process, a molecular system was built consisting of 10 polyethylene chains, each containing 100 monomers $[-C_2H_4-]$, one of which is shown in Fig. 1. Then, 100 O_2 molecules were added to this molecular system.

For modeling and analysis of the obtained polyethylene+ O_2 (PE+ O_2) structure, the Material Studio software suite [1] was used. Material Studio is a powerful molecular modeling software that enables users to create, visualize, and optimize material models at the atomic and molecular levels. Thanks to its wide range of tools, this software facilitates detailed analysis of molecular geometry, calculations of physicochemical properties, and simulation of processes occurring within materials.

Material Studio is based on methods of quantum chemistry and molecular dynamics, which are key for accurately modeling polymer systems, such as high-density polyethylene. Thanks to this software, it is possible to investigate the bonding mechanisms between polymer chains, analyze the impact of synthesis on the material's final properties, and determine the optimal conditions for its production. Additionally, Material Studio enables modeling the behavior of polymers under various thermodynamic conditions, thereby facilitating the development of innovative solutions for the industrial application of high-quality materials.

Thus, the use of Material Studio not only simplifies the process of constructing and analyzing molecular models but also opens up new opportunities for optimizing the synthesis and modification technologies of polymer materials, which is extremely important in modern research and practical applications.

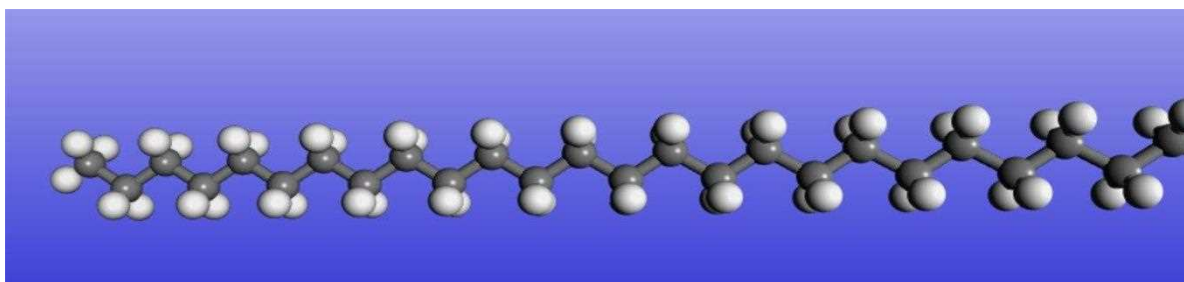


Fig.1. Amorphous structures of PE molecular systems constructed in Materials Studio.

Force fields and molecular system models

To achieve realistic results, it is important to correctly select the interatomic potentials, as they mathematically describe the forces acting within molecular systems. Next, we will examine how chemical force fields, or interatomic potentials, provide this description and the factors that influence their selection and parameterization.

Chemical force fields, or interatomic potentials, are typically described by specific mathematical functions, with parameters generally obtained empirically—except in cases where coefficients derived from an *ab initio* approach, that is, based on quantum mechanics, are used. Potentials can vary in terms of the chosen mathematical dependencies that describe them, as well as according to the chemical composition of the substances under study, the level at which chemical reactions are considered, and the degree of detail of the molecular systems to which they are applied.

According to the degree of detail, molecular systems can be divided into three types of models [2]:

- explicit atom (EA);
- united atom (UA);
- coarse-grained, (CG).

The EA model provides the most detailed representation of the physical system's structure; however, the complexity of many studied molecular systems necessitates the use of simplified approaches to extend the spatial and temporal scales of modeling and/or reduce the computational resource requirements. The UA model involves combining hydrogen atoms with the atoms of other elements attached to them into a single unified particle, which is modeled using the corresponding interaction potential [3]. For detailed modeling of the behavior of such polymer systems, it is extremely important to account for interatomic interactions, which is ensured by the use of force fields.

Force fields, or interaction potentials, are fundamental elements in the modeling of molecular systems, as they describe how atoms and molecules interact with one another. The correct selection and tuning of force fields are critically important for accurately representing the physical properties of a system – from energy distribution to determining the stability of structures and the reactivity of molecules. Different force fields can be specialized for modeling various types of interactions – from simple van der Waals forces to complex reactive potentials that account for the breaking and forming of chemical bonds.

Using Materials Studio, a PE+O₂ molecular system was constructed and, with the attached CVFF force field, subjected to geometric optimization and energy minimization, and then equilibrated under an isochoric-isothermal NVT ensemble for 5 ns. Afterwards, the PE+O₂ model was converted into a data file for input into the LAMMPS program.

LAMMPS and pyrolysis simulation

LAMMPS (Large-scale Atomic/Molecular Massively Parallel Simulator) [4] is one of the most popular programs for conducting molecular dynamics simulations, thanks to its high efficiency and ability to handle large systems containing millions of atoms. Its flexibility allows users to integrate various force fields, adapting them to specific tasks and types of studied systems. This is especially important for environmental research, where modeling processes at the atomic level can help to understand the mechanisms of pollutant formation, their interaction with the surrounding environment, and the development of methods for their neutralization.

The combination of LAMMPS' powerful capabilities with carefully selected force fields enables the creation of highly accurate models that reflect the dynamics of molecular processes in natural ecosystems. This approach not only contributes to a deeper understanding of fundamental processes but also opens new prospects for the development of innovative technologies in environmental safety and sustainable development. LAMMPS is used as a powerful tool for molecular dynamics simulations in such cases, and thanks to its efficiency and scalability, it allows for detailed modeling of pyrolysis processes, enabling the analysis of the dynamics of gas product formation at the atomic level.

To model the pyrolysis process in LAMMPS, a corresponding script was created in which, after reading the PE+O₂ data file, the ReaxFF force field [5] is attached, and the pyrolysis process is set up using an NVT ensemble at a temperature of 1000 °C for 200 ps with a time integration step of 0.5 fs. Fig. 2 shows the evolution of the formation of intermediate gaseous products and substances over time, as observed during the pyrolysis simulation at 1000 °C. Changes in the concentrations of gaseous molecules begin with the onset of interaction with molecular oxygen. The initial time is defined as the moment when the oxygen concentration started to drop sharply, after which it continuously decreased to zero. As for the gaseous intermediate products and the formed substances, their concentrations initially changed rapidly and eventually stabilized around a certain value. The main gaseous products of polyethylene pyrolysis were hydrogen (H₂), methane (CH₄), ethane (C₂H₆), ethylene (C₂H₄), acetylene (C₂H₂), and carbon monoxide (CO) at 1000 °C. The quantitative values of the pyrolysis reaction products obtained from the MD simulation agree within 10–15% with the data from [6].

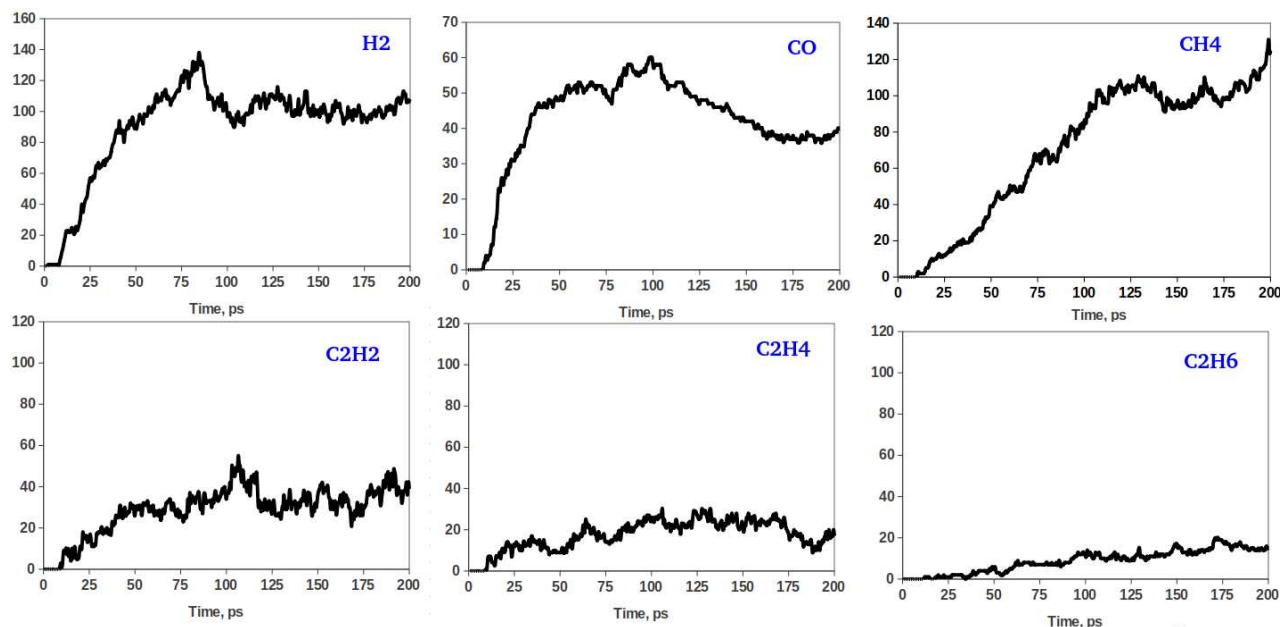


Fig.2. Variation in the numbers of gaseous product molecules in the system at 1000 °C

Conclusions

The integration of MD simulations with experimental research reduces the time and resources required for laboratory tests, while providing highly accurate process analysis. This approach is particularly important for addressing pressing environmental issues such as air, water, and soil pollution, as well as for predicting the impact of anthropogenic factors on climate and biodiversity.

Thus, MD modeling opens new prospects for environmental research by promoting a deeper understanding of natural processes and stimulating the development of innovative technologies for environmental protection and sustainable development. Further studies will focus on integrating molecular dynamics simulations with experimental research to validate and improve the models.

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Modeling the Operation of Glass Furnaces in Order to Optimize Technological Processes

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Abstract. *In the work, computer modeling of thermal processes in the furnace was carried out, heat balances were calculated and analyzed, and the performance of the furnace was analyzed after improving the technological regimes. This will allow you to select the optimal design and operating parameters of the glass melting furnace.*

Keywords: glass furnace, regenerators, combustion, electric heating, computer simulation of technological processes.

Introduction

The making of industrial silicate glass takes place at a temperature of about 1500 °C. Traditionally, the energy used to operate the glass furnace was provided mainly by fossil fuels [1]. At the same time, more than 75 % of the total energy required for the production of glass products is consumed by the melting furnace. Therefore, increasing the efficiency of glass furnaces is the subject of constant research on improving the technological modes of their operation [2, 3]. Due to the urgent need to reduce greenhouse gas emissions, the main attention of design engineers is directed to the further optimization of glass melting processes. In fact, the only way to reduce CO₂ emissions is to reduce energy consumption [4]. The difficult situation with energy resources forces us to fundamentally change the policy of energy consumption in industry, including at enterprises of the glass industry. The experience of foreign countries shows that the creation of a highly efficient and competitive industrial sector is possible only by reducing energy costs per unit of production [5, 6].

Materials and Methods

To simulate the operation of glass furnaces, we used the OptimaGlassfurnace program we developed. In the study, we changed the following parameters:

- furnace performance;
- energy resources (type of fuel, calorific value, power of additional electric heating);
- charge (charge consumption per 1 kg of glass mass, yield of degassing products of the charge, chemical composition of degassing products, humidity of the charge);
- glass mass (theoretical heat consumption for making 1 kg of glass mass, which consists of heat consumption for the processes of silicate and glass formation, physical heat of the conditioned glass mass, heat of heating the products of degassing; glass melting heat, and also taking into account the heat capacity of the glass mass, the maximum boiling temperature, temperature at the bottom of the pool, temperature of production of flow coefficient (Novak number));
- combustion process (temperature of flue gases (flame temperature), degree of blackness of the flame, temperature of spent flue gases, temperature of air entering combustion, air consumption per 1 m³ (n. c.) of natural gas, output of flue gases per 1 m³ (n. c.) of natural gas and the chemical composition of combustion products);

- overall dimensions of the furnace (dimensions of the furnace basin, dimensions of the flame space, dimensions and number of inlets of burners, and loading pockets);
- laying of the main fences of the furnaces (separate data on four characteristic areas of the furnace: vault, walls of the flame space, walls of the pool, bottom of the pool. Type of refractory and heat-insulating layer, their thickness, coefficient of thermal conductivity) [7].

The OptimaGlassfurnace program allows for the identification of items of unproductive heat energy consumption and outlines ways to minimize them. In addition, it allows to vary any initial parameter and at the same time analyze the change in the resulting characteristic. This makes it possible to carry out theoretical research on obtaining generalized data on the influence of one or another factor on the technical and economic characteristics of the furnace, as well as to solve optimization tasks. It is possible to introduce additional parameters and make calculations for two masonry options: the first, a furnace without additional insulation, the second, a furnace with additional high-efficiency thermal insulation (Fig. 1).

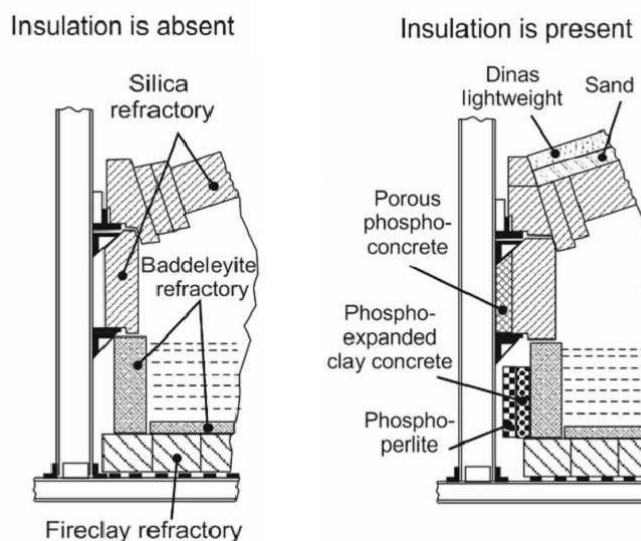


Fig.1. Insulation diagrams for glass melting furnaces.

Two variants of furnaces with a capacity of 100 t/day were chosen for simulation. The first option with a specific removal of glass mass of 1000 kg/(m²·day) (a furnace with a transverse flame direction is adopted), the second with a specific removal of glass mass of 2000 kg/(m²·day) (a furnace with a horseshoe-shaped flame direction is adopted) (Fig. 2).

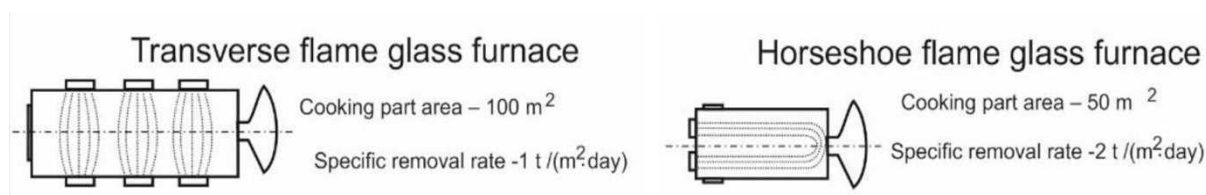


Fig.2. Furnace characteristics.

Also, for these options, additional parameters were introduced – two masonry options (the first – a furnace without additional insulation, the second – a furnace with additional high-efficiency thermal insulation). It is also possible to take into account the thickness of effective thermal insulation for individual elements of the furnace enclosure; the temperature of the heated air; share of heat, which is introduced at the expense of electricity. Processes were simulated according to the set parameters, and the following information was obtained:

- gas consumption;
- furnace efficiency;

- profitable articles of the heat balance in absolute values and in percentage terms;
- expenditure items of the heat balance in absolute values and in percentage terms;
- values of heat losses through individual sections of the glass furnace enclosure (in absolute values and in percentage terms);
- temperature distribution in the lining of the furnace fences (in a multi-layer wall).

Results and Discussion

Studies have confirmed that the most significant item of energy loss is heat carried away by flue gases (about 60 %). These losses cannot be called irrecoverable losses. Part of this heat is returned with the air coming from the regenerators for combustion.

In second place in the cost items are the costs for the glass formation process. They make up 21 % and refer to productive costs. In third place are heat losses due to the furnace enclosure. Their share varies from 5 % to 11 %. The first value refers to a furnace with a large specific removal without thermal insulation, the second to a furnace with a small specific removal and thermal insulation. Intermediate values occur in furnaces with a large specific removal, but without thermal insulation – 8 %, and with a small specific removal, but with thermal insulation – 7 %. Thus, increasing the specific removal of glass mass by two times (and at the same time reducing the main dimensions of the furnace), in terms of reducing losses through the walls of the furnace, is similar to the use of effective thermal insulation of the original low-performance furnace.

In the fourth place, losses due to furnace openings. They amounted to 6–7 % for a large low-performance furnace and 3–4 % for a small high-performance furnace. In the last place are losses with reverse convection flow. This value is up to 4 %. With an increase in the share of electricity input for heating the furnace, the total specific energy consumption for boiling glass increases along a certain concave curve. (Fig. 3).

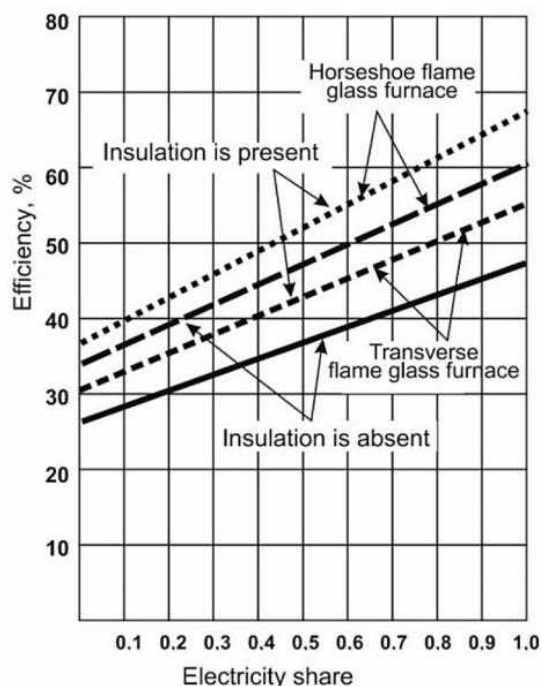


Fig. 3. The effect of additional electric heating on the efficiency of a glass melting furnace.

Increasing the air heating temperature in the regenerators reduces the specific gas consumption per 1 kg of glass and increases the efficiency of the furnace. Thus, when the air temperature increases from 700 to 1200 °C in a non-insulated furnace with low specific removal, gas consumption can be reduced from 0.41 to 0.27 m³/kg, and the efficiency can be increased from

21 to 34 %. For a heat-insulated furnace with a high specific removal of glass mass, the gas consumption was reduced from 0.28 to 0.19 m³/kg, and the efficiency increased from 31 to 47 %. Increasing the air heating temperature by 100 °C increases the efficiency by 26–32 %.

Having analyzed the data of the conducted analysis, it can be stated that the most effective, from the point of view of increasing the energy efficiency of the glass furnace, is the introduction of additional electric heating for the furnace with a low specific removal of glass mass and without thermal insulation [8].

A slightly lower efficiency of additional electric heating is characteristic of furnaces with high specific removal of glass mass and sufficient thermal insulation. The indicators of furnaces with low specific removal of glass mass (transverse flame) with thermal insulation and with high specific removal of glass mass (horseshoe flame) without thermal insulation occupy an intermediate value.

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The Influence of Channel Curvature and Spacer Geometry on Flow Characteristics in Membrane Module Channels

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Abstract. *The efficiency of membrane processes depends on the hydrodynamic conditions within the channels of membrane modules, particularly the channel curvature and spacer configuration. This study focuses on analyzing the influence of membrane module element curvature on hydrodynamic characteristics using computational fluid dynamics (CFD).*

Keywords: spacer, membrane, reverse osmosis (RO), FreeCad, CFD (Computational Fluid Dynamics), channel curvature.

Introduction

Membrane technologies are widely used in various industries, including food, pharmaceutical, and water treatment, due to their ability to efficiently separate mixture components [1]. However, the efficiency of these processes depends on the hydrodynamic conditions within the membrane module channels. For instance, channel curvature can significantly affect flow characteristics, which may influence mass transfer processes and the overall system performance [2].

The geometry of membrane module channels plays a crucial role in shaping hydrodynamic conditions. In particular, the presence of curvature in the channels can influence velocity and pressure distribution, as well as the flow regime (laminar or turbulent). Studies show that certain geometric configurations can enhance mixing and reduce stagnant zones, which positively impact mass transfer processes and lower the risk of membrane fouling [2].

Given the above, the aim of this study is to analyze the impact of channel curvature on the hydrodynamic flow characteristics in membrane modules with spacers. Specifically, the research will investigate whether variations in curvature radius and channel shape affect velocity distribution, pressure, and flow turbulence.

In this regard, numerous studies in recent years have focused on the influence of spacers on nearly all commercial membrane processes. It is important to note that most of these studies have evaluated spacer efficiency using computational fluid dynamics (CFD) methods [1-2].

Flow modeling in membrane modules is a key aspect for understanding and optimizing their performance. Several approaches to modeling exist, including mathematical modeling, computational fluid dynamics (CFD), and experimental modeling [2].

Spacers are important components of membrane modules, responsible for the flow of feed through the membrane. The spacer configuration within the channel significantly affects the hydrodynamic and mass transfer characteristics of the process, as well as fouling, and promotes flow turbulence. Their impact on hydrodynamics is considerable. A poorly selected spacer increases hydraulic resistance and can create stagnant zones. Optimizing spacer design is crucial to achieve a balance between improved mass transfer and minimizing energy consumption [3].

This work will explore methods for studying the impact of channel curvature on flow characteristics in membrane modules with spacers, focusing on the use of computational fluid dynamics (CFD).

Computational fluid dynamics (CFD) is a powerful tool for analyzing and predicting fluid behavior in complex geometries, such as membrane module channels with spacers. CFD allows for detailed investigation of velocity distribution, pressure, and other flow parameters without the need for expensive and time-consuming experiments [1].

Specialized software packages are used for modeling, solving the Navier-Stokes equations for incompressible fluids. The modeling process includes creating the geometric model of the channel, generating the computational mesh, setting boundary conditions and flow parameters, as well as performing numerical calculations followed by result analysis. In this work, the model solution was obtained using the OpenFOAM-v2212 software package, which was integrated into the FreeCAD 3D design system.

The preliminary evaluation of the impact of curvature on flow characteristics in the membrane channel was performed visually by comparing velocity field visualizations, created in the ParaView 5.10.1 software environment. Figures 1 to 3 show some of these visualizations. Specifically, the velocity field in the transverse cross-section, taken at the middle length of the channels, is shown in Figure 1. Figure 2 demonstrates the velocity field in the longitudinal section, taken at the middle cross-section of the flat channel height and the central radius of the curved channels. Figure 3 presents the pressure field. The results presented in this study were obtained for a cell size of $0.05 \cdot 10^{-3}$ m (0.05 mm).

No significant differences were observed in the obtained results, where the discrepancies for the real and ideal spacer thread shapes were easily visible. The velocity field also corresponds to laminar flow conditions, with the maximum velocity at the center of the channel and a gradual decrease near the walls. It is worth noting that at the boundary surfaces, the velocity fields also appear similar.

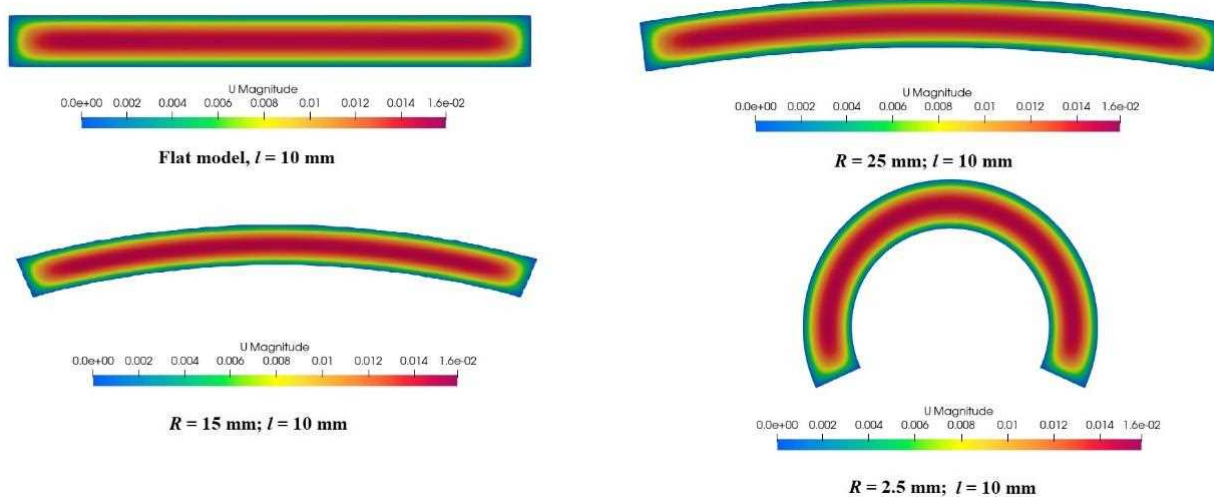


Fig. 1. Velocity fields in the transverse cross-sections of some of the studied channels.

Therefore, the flat model can be considered a reasonable approximation of the spiral module channel. However, all these studies were conducted for hypothetical channels without spacers. Since the curvature of the spacer can affect the magnitude of hydraulic resistance, this issue is considered the objective of our further research.

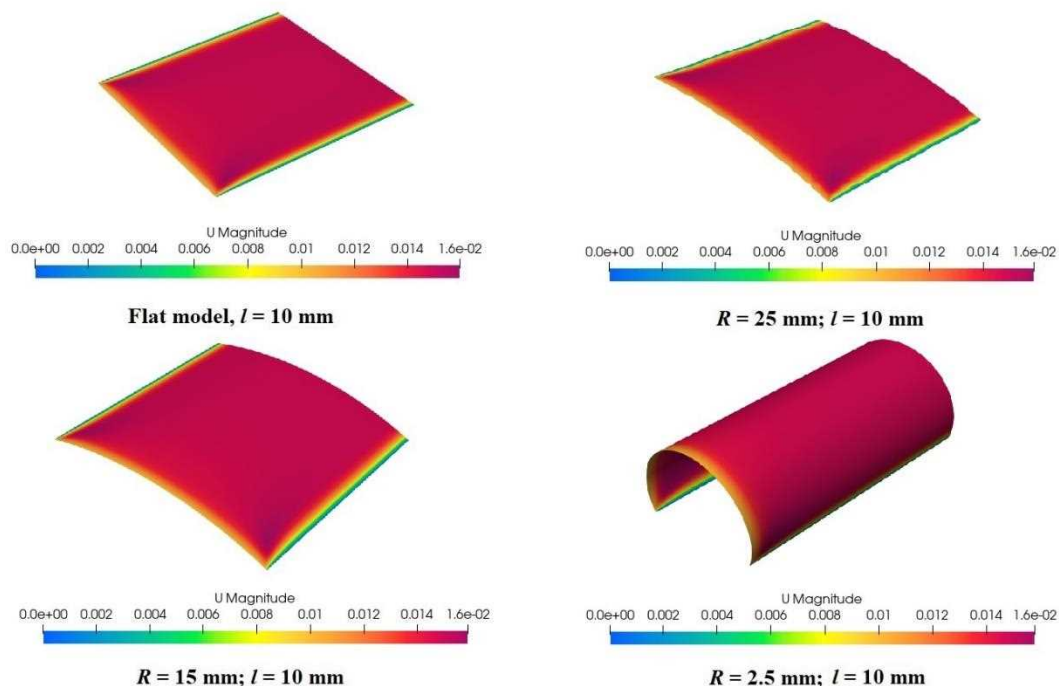


Fig. 2. Velocity fields in the longitudinal cross-sections of some of the studied channels.

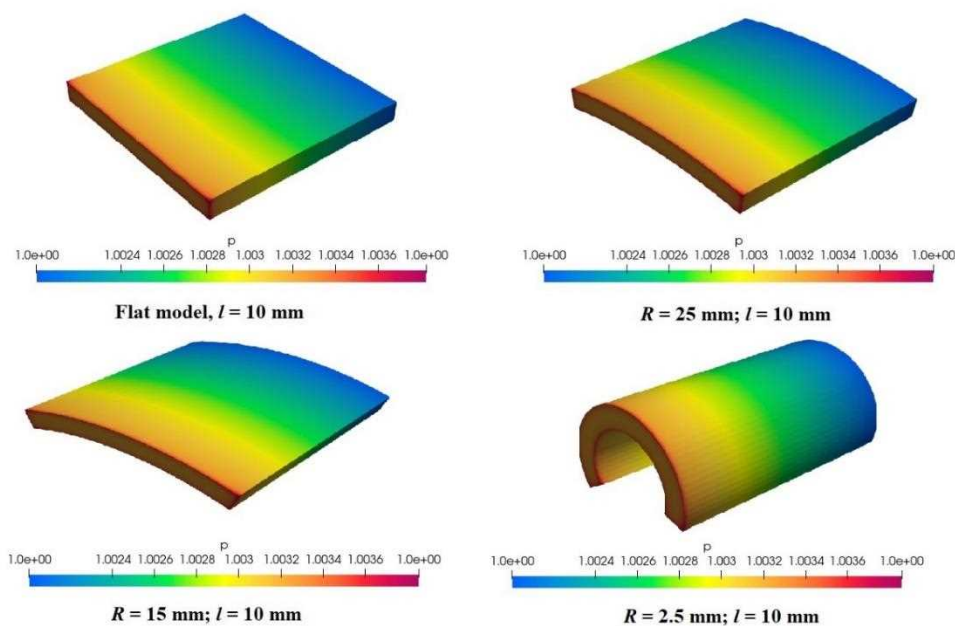


Fig. 3. Velocity fields in the longitudinal cross-sections of some of the studied channels.

To verify the impact of spacer curvature, trial simulations of flow were conducted in both the flat and curved models, with the visualization of the results shown in Figures 4 and 5. As in the case with hypothetical channels without spacers, the velocity fields appear very similar in this case. However, for final conclusions regarding the acceptability of the flat model, further research and analysis of quantitative parameters, particularly hydraulic resistance, are required.

Conclusions

The study showed that the flat model can be considered a reasonable approximation of the spiral module channel. However, all these studies were conducted for hypothetical channels without spacers. Since the curvature of the spacer can influence hydraulic resistance, this issue is

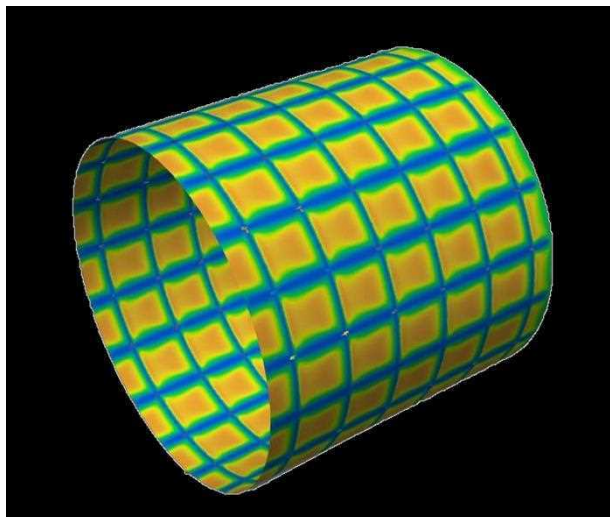


Fig. 4. Visualization of the velocity field in the curved membrane channel model with spacers.

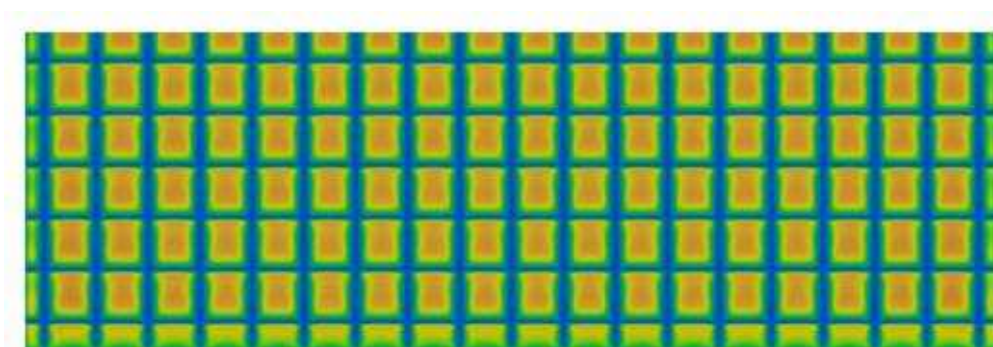


Fig. 5. Visualization of the velocity field in the flat membrane channel model with spacers.

considered the objective of our further research. The preliminary results obtained show that the velocity field visualizations appear very similar. However, for final conclusions regarding the acceptability of the flat model, further research and analysis of quantitative parameters, particularly hydraulic resistance, are necessary.

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Molecular Modeling of Polymethylmethacrylate-Polyaniline Composites and Study of Its Properties

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Abstract. *Polymer-polymer composites based on polyaniline and polymethylmethacrylate were obtained. It was shown that intermolecular hydrogen bonds are formed between the composite components. The energy of hydrogen bonds is determined. The intermolecular interaction between the components of the polymer-polymer composite affects its physicochemical parameters.*

Keywords: polyaniline, polymethylmethacrylate, hydrogen bonds, electrical conductivity, thermo-mechanical properties.

Composites based on polyaniline and water-soluble polymers are promising for the production of bio- and chemosensors [1 - 3]. Composites based on polymethylmethacrylate and polyaniline have not been studied sufficiently. Due to the electrically conductive component and good film former, such composites can be used as anti-corrosion agents [4]. Composites based on polyaniline (PANI) and polymethylmethacrylate (PMMA) have a number of interesting properties that allow them to be used in practice. PMMA has good film-forming properties, and PANI has electrical conductivity, which makes such composites promising materials for corrosion protection.

Quantum-chemical calculations were carried out for the starting polymers and polymer-polymer composites (PPC). Quantum-chemical calculations were carried out for PMMA (8 units) and PANI (6 protonated units), their compositions were carried out using the MOPAC2016 program and the WINMOSTAR graphical interface, using the semi-empirical method PM7.

Thermodynamic calculations of the models were performed using the key parameter THERMO(290.330.10). Quantum chemical studies of PANI have shown that the molecule is strongly polarized and can form many conformations. A fragment of the PANI macromolecule, which contains 6 units for one of the conformations, is shown in Fig. 1.

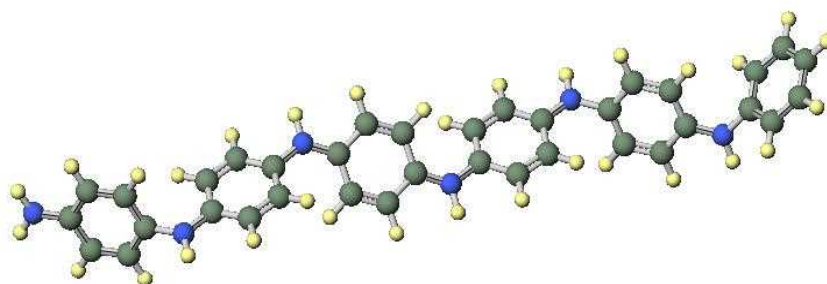


Fig.1. Fragment of the PANI macromolecule.

Figure 2 shows a fragment of an 8-membered PMMA macromolecule.

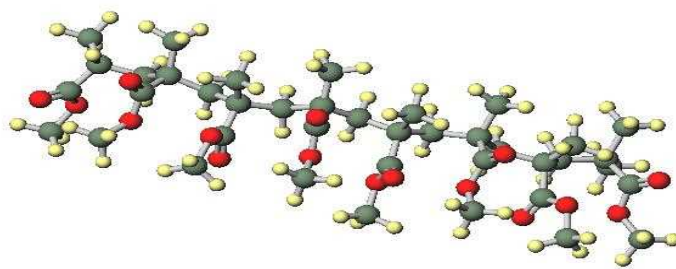


Fig. 2. Fragment of the macromolecule PMMA.

It should be noted that the macromolecules that make up the composite can have many conformations. During the formation of the composite, the conformations of the initial components will change. A Fragment of the model of the PANI-PMMA composite is shown in Fig. 3.

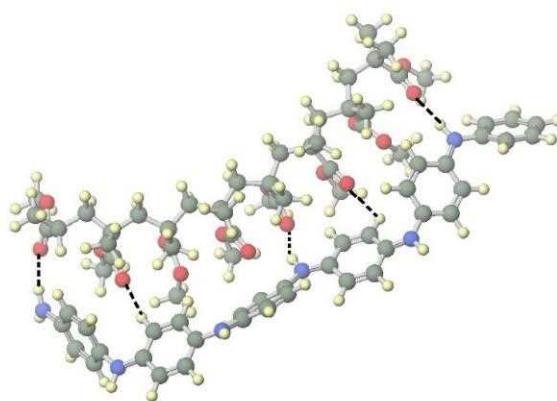


Fig. 3. Fragment of the model of the PANI-PMMA composite (lines - hydrogen bond).

The calculated values of the heat of formation for the composite are lower than the sum of the corresponding values of the investigated polymers. The decrease in the heat of formation is associated with the formation of hydrogen bonds between PMMA and PANI fragments.

The hydrogen bonds formed in PPC affect physicochemical parameters. The information about the formation of hydrogen bonds for a fragment containing 8 PMMA macromolecule fragments and 6 PANI fragments can be extended to larger macromolecules. It should be noted that due to the change in the conformation of both macromolecules, some of the hydrogen bonds are broken, while there is a possibility of hydrogen bonds forming in other places.

The study of thermo-mechanical curves indicates that connections are formed between the components, and the shape of the initial curves of PANI, PMMA and PPC is different (Fig. 4)

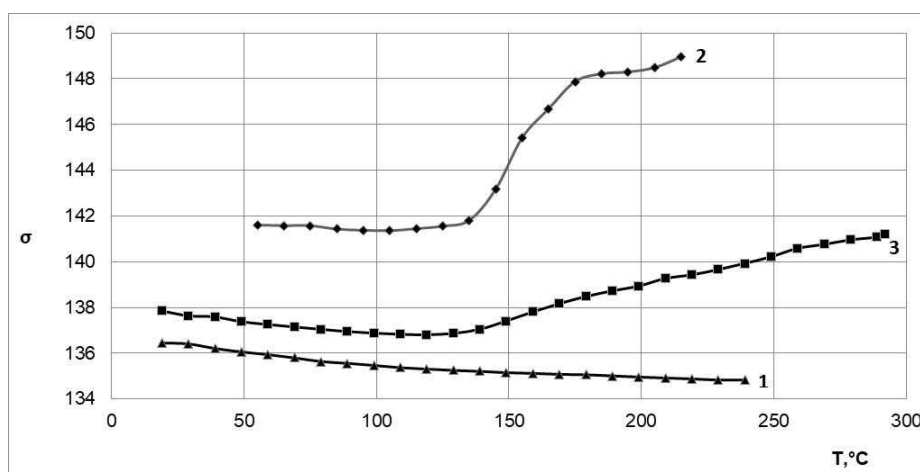


Fig. 4. Thermo-mechanical curves of PANI (1), PMMA (2) and composite (3).

The different shape of the curves indicates the interaction between the components of the PPC. Studying the electrical conductivity of PPC as a function of the content of the conductive PANI-PMMA and the temperature made it possible to calculate the activation energy of charge transfer, E_a (Table 1).

Table 1

The dependence of the specific resistance and electrical conductivity of polymer-polymer composites on the PANI-PMMA ratio

PANI-PMMA, %	l , mm	ρ , $\Omega\cdot\text{m}$	σ , $\text{Sm}\cdot\text{m}$	E_a , eV
100 – 0	4	48.24933	0.020726	1.773
90 – 10	3	22.28724	0.044869	1.713
80 – 20	3.5	9.923357	0.100772	1.503
70 – 30	4	8.720248	0.114676	1.495
60 – 40	3	8.316174	0.120248	0.991
50 – 50	2	8.26822	0.120945	0.988
40 – 60	3	6.654378	0.150277	0.623
30 – 70	2.5	5.565292	0.179685	0.42
20 – 80	3.5	16.43044	0.060863	1.682

The numerical values of the charge transfer activation energy are in the range of 0.42 – 1.773 eV. Such values of E_a indicate a semiconductor mechanism of electrical conductivity in composites. The composite containing 90% PMMA and 10% PANI is practically not electrically conductive. The dependence of the specific electrical conductivity on the composition of the composite is shown in Fig. 5.

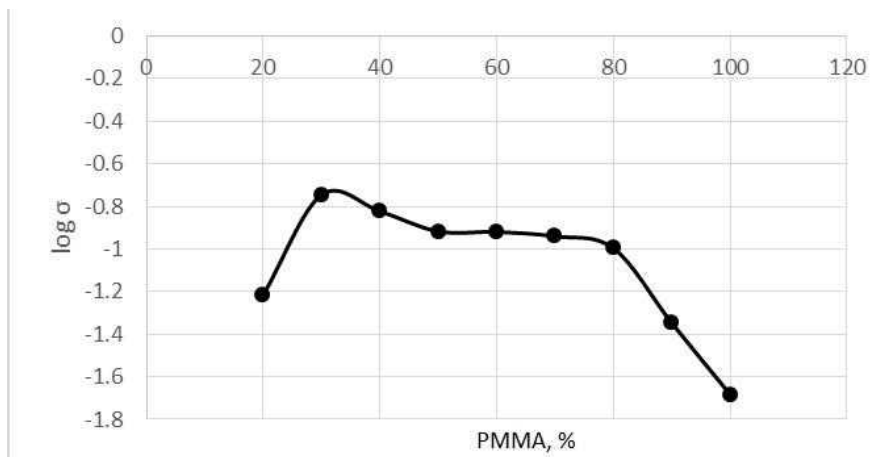


Fig. 5. Dependence of the logarithm of the specific electrical conductivity on the mass concentration of PANI.

The obtained results of measurements of electrical conductivity of composites with different contents of PANI and PMMA showed that the dependence of specific electrical conductivity on the composition of the composite is complex. (Fig. 5).

The study of the thermal stability of composites shows that there is a relationship between the components, and the composition of the composite affects the shape of the curves (Fig. 6). The process of thermal decomposition of composites is complex and occurs in several stages.

The study of X-ray and FTIR spectra confirms the conclusion about the interaction between the macromolecules of polyaniline and polymethylmethacrylate in the composite.

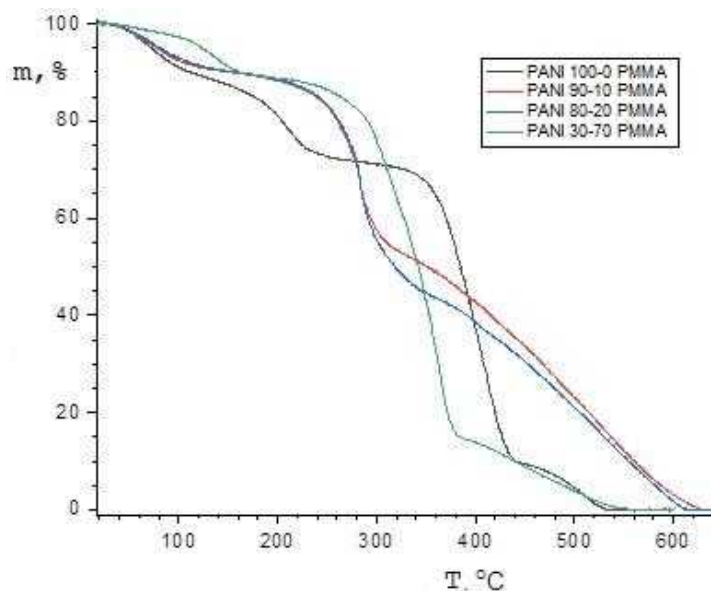


Fig. 6. The curve of loss of polymers during heat treatment.

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DEVELOPMENT, ENERGY AND RESOURCE SAVING IN THE CHEMICAL AND FOOD TECHNOLOGIES

Design and Development of a High-Concentration Aqueous Ammonia Solution Production Plant

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Abstract. *The development and optimization of a high-concentration ammonia water production process is presented, focusing on energy-efficient equipment and two-stage ammonia absorption. The system enhances nitrogen fertilizer production for agriculture, ensuring effective gas-liquid separation, minimizing energy consumption, and maintaining product quality.*

Keywords: ammonia water, nitrogen fertilizers, absorption column, agriculture, chemical production.

Introduction

Aqueous ammonia solutions, in which it exists predominantly in the form of ammonium hydroxide (NH_4OH) [1], are called ammonia water [2]. The solubility of NH_3 in water is extremely high - about 1200 volumes (at 0 °C) or 700 volumes (at 20 °C) in the volume of water [3,4].

Ammonia water ($\text{NH}_3 \text{ H}_2\text{O}$) is a transparent, colorless, or slightly yellowish solution of gaseous ammonia in water. It has a strong odor and is non-flammable. However, during degassing, ammonia vapors can accumulate and reach explosive concentrations in enclosed spaces [5]. Gaseous ammonia released from aqueous ammonia is, under normal conditions, a gas with a pungent odour, explosive, toxic, and flammable.

In industry, an aqueous solution of ammonia is obtained by the absorption of synthetic ammonia with chemically demineralized water [6]. Ammonia is used in various concentrations [7, 8]. A 10% solution of ammonia is known as ammonia, which is widely used in medicine. An aqueous solution of technical ammonia contains up to 30% ammonia. Aqueous ammonia of special purity (with a concentration of at least 25% by weight) must be manufactured according to the requirements of DSTU ISO 7108:2005 «Technical ammonia solution. Determination of ammonia content by the titrimetric method (arbitration method). Technical aqueous ammonia must be prepared according to the requirements of ISO 7108:1985 «Ammonia solution for industrial use». Depending on the purpose, technical aqueous ammonia is produced in two grades: A - for various industries (the mass fraction of ammonia is not less than 25%); B - for agriculture as a nitrogen fertilizer (the mass fraction of ammonia is not less than 25%, in terms of nitrogen not less than 20,5%).

Aqueous ammonia is commonly used in the chemical industry for producing nitrogen fertilizers [9]. Aqueous ammonia, like other liquid nitrogen fertilizers, is used as a primary fertilizer for all crops [10]. Producing aqueous ammonia is 30-40% cheaper than producing solid fertilizers since such technological operations as granulation, drying, sorting, and conditioning of the product are eliminated. The cost of one unit of active substance in ammonia water is 1.5 to 2 times cheaper than in ammonium nitrate. Ammonia can evaporate from aqueous ammonia, leading to nitrogen loss during transportation, storage, and application.

Literature Review

It is known that the main methods for the preparation of an aqueous ammonia solution (ammonia water) and also catching emissions of ammonia from departing gases are based on the absorption of gaseous ammonia water (Fig. 1) [11]. Raw materials (gaseous ammonia) are supplied under redundant pressure of 0.2 MPa from the synthesis shop, ammonia or liquid ammonia storage, into the absorption column A-1 with cap plates. It also releases gaseous ammonia released when the tanks are filled with liquid ammonia [12]. To avoid clogging columns with hardness salts, the absorption of ammonia is produced in chemically purified water that is served from the collection of chemically purified water S-1 to the top plate columns A-1. Lower Part Column A-1 represents by yourself a tubular heat exchanger designed for the removal of significant parts of the heat of ammonia solution. Through the heat exchanger tubes, reverse cooling water is cooled in the apparatus air cooling ACU-1. Water ammonia circulates in the intertube space, through the layer bubbling gaseous ammonia. The remaining unabsorbed ammonia enters the upper part columns, where gas passes through bubble cap plates. On the plates can be located cooling serpentine in which water circulates. Production of water ammonia (25% NH_3 concentration) is pumped from columns A-1 with pumps into collection S-1 and further into aqueous ammonia storage T-2.

Gaseous ammonia is released from storage T-2 and collection S-1 for long-term storage of aqueous ammonia. As a result, exposure to ambient heat air and solar radiation is directed back to absorption in column A-1. From storage tanks, aqueous ammonia is pumped into railway and automobile tanks for transportation to consumers.

In nitrogen production technology, industrial methods for obtaining technical ammonia water are considered (ammonia mass fraction not less than 25%, in terms of nitrogen not less than 20.5%).

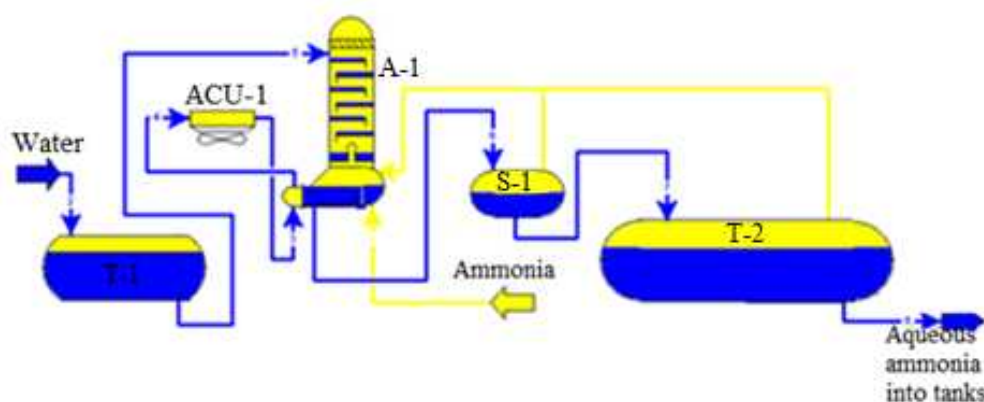


Fig. 1. Flow chart for obtaining aqueous ammonia:

T-1 – collection chemically purified water; ACU-1 – apparatus air cooling negotiable water; A-1 – absorber; S-1 – aqueous ammonia collector; T-2 – aqueous ammonia storage; 1 – gaseous ammonia from the synthesis workshop or storages liquid ammonia; 2, 5 – chemically demineralized water (absorbent); 3, 4 – cooling recycled water; 6, 7, 8 – aqueous ammonia solution (ammonia water).

Research Methodology

A continuous method for obtaining a high-concentration aqueous ammonia solution (with an ammonia mass fraction of 45-50% and nitrogen content of at least 32%) [13], based on a two-stage disammonia solution and saturation solution, and at the second stage gaseous ammonia from the first steps dissolved in the original water in isothermal conditions, and on the first degrees liquefied or part evaporated ammonia dissolve in adiabatic conditions in ammonia water that comes from the second degree.

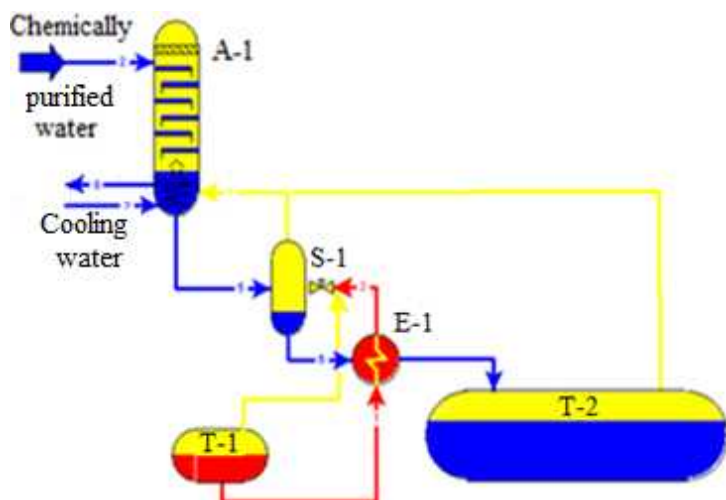


Fig. 2. Flow chart of production ammonia water high concentrations:

T -1 – vessel of liquefied gas ammonia; E -1 – refrigerator-evaporator; A-1 – absorber; S -1 – mixer -separator; T -2 – storage of aqueous ammonia; 1 – liquefied ammonia; 2 – chemically demineralized water (absorbent); 3 – gas-liquid mixture of ammonia; 4 – gaseous ammonia from mixer -separator and storage of aqueous ammonia in the absorber; 5 - diluted ammonia water; 6 - concentrated aqueous ammonia solution (ammonia water).

The heat of absorption is removed by cooling water, which is passed through the built-in or remote heat exchangers devices. In the absorber A-1, diluted ammonia water.

In the evaporator refrigerator E-1, the concentrated aqueous ammonia solution from mixer-separator S-1, due to heating and partial evaporation, liquefied ammonia from tank T-1, with its subsequent throttling before feeding into the mixer-separator S-1. From the refrigerator-evaporator E-1, cooled aqueous ammonia solution is drained into the T-2 storage.

Gaseous ammonia, which is displaced from the T-1 vessel when it fills liquid ammonia, is sent to the mixer-separator S-1 and then to the absorber A-1, in which it is absorbed by water. Respiratory gases from aqueous solution storage ammonia T-2 are fed into absorber A-1.

Given the concentration of ammonia in water, as supported by regulation, correlation submissions, absorption of water and liquid ammonia with temperature correction, ammonia water at the outlet from the mixer-separator S-1.

This method can be used to obtain an aqueous ammonia solution (ammonia water) with a content of up to 45-50% dissolved ammonia. In this case, the amount of heat absorbed during the evaporation of liquid ammonia is fully used in the technological process. The pressure in the mixer-separator S-1 corresponds to the hydraulic resistance of the absorber A-1 with gas ducts and does not exceed 0.05 MPa. As a result, ammonia water is obtained without the use of electricity to drive pumps and without the use of external sources of cold, the production of which is also an energy-intensive process.

Results and discussion

Indeed, the efficiency of the absorption of ammonia by water significantly depends on temperature, which is associated with a decrease in solubility with increasing temperature. At the same time, the solubility of ammonia in water increases with increasing pressure (Table 1).

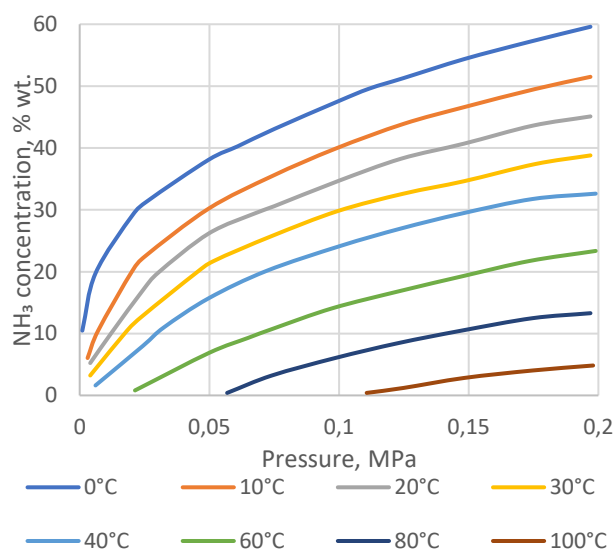
According to the proposed method (Fig. 2) [14], in the separator-mixer S-1 (first stage absorption) are served weak aqueous ammonia solution from absorber A-1 and gas-liquid mixture of ammonia from the evaporator refrigerator E-1. When mixing liquid ammonia, it evaporates with the absorption of heat, and at the same time, ammonia dissolves in ammonia water with the release of heat. As a result, concentrated aqueous ammonia solution and gaseous ammonia. Gaseous ammonia is fed into the absorber A-1, and the concentrated aqueous solution is cooled in the evaporator refrigerator E-1.

In absorber A-1 (second degree absorption), with mixer - separator S-1 enters gaseous ammonia.

Table 1

Solubility of ammonia in water at various pressures and temperatures

Pressure, MPa	Temperature, °C										
	-30	-20	-10	0	10	20	30	40	60	80	100
0.02	0.431	0.364	0.306	0.253	0.202	0.155	0.11	0.068	-	-	-
0.05	0.567	0.475	0.406	0.347	0.294	0.244	0.197	0.152	0.071	-	-
0.1	0.856	0.615	0.512	0.438	0.378	0.325	0.225	0.208	0.14	0.062	-
0.15	-	0.813	0.599	0.503	0.433	0.384	0.332	0.286	0.193	0.166	0.033
0.2	-	-	0.701	0.566	0.483	0.418	0.363	0.314	0.225	0.141	0.067
0.25	-	-	0.868	0.627	0.526	0.454	0.396	0.345	0.255	0.17	0.091
0.3	-	-	-	0.702	0.568	0.487	0.424	0.371	0.28	0.195	0.115
0.4	-	-	-	0.930	0.790	0.547	0.473	0.414	0.318	0.234	0.154
0.5	-	-	-	-	0.971	0.611	0.52	0.453	0.35	0.265	0.186
0.6	-	-	-	-	-	0.651	0.564	0.490	0.379	0.292	0.214
0.8	-	-	-	-	-	0.935	0.670	0.560	0.429	0.336	0.257
1	-	-	-	-	-	-	0.824	0.630	0.473	0.372	0.29



From the analysis of reference data on the phase equilibrium of gas-liquid binary systems, as well as the graphical dependences of the equilibrium pressure of saturated vapors over an aqueous ammonia solution (ammonia water) at different concentrations and temperatures constructed according to Henry's law (Figs. 3, 4), which describes the solubility of gas in a liquid, it follows that theoretically stable ammonia water with an ammonia concentration of 34% by weight and above can be obtained only at temperatures below 10 °C. At 20-22 °C, a maximum concentration of about 30% can be obtained. A solution of such concentration should be stored at a pressure (absolute) not lower than 0.2 MPa (overpressure 0.1 MPa). (Fig. 5).

Storage and application of liquid nitrogen fertilizers traditionally occurs under conditions close to normal environmental conditions (temperature $T=20^{\circ}\text{C} = 293\text{ K}$, pressure $P = 0.1013\text{ MPa}$), which is due to the concentration of aqueous ammonia (about 25%), which is produced by the nitrogen industry, since the solution remains stable even at 32°C and under atmospheric pressure in the storage tank.

Based on reference data on the thermophysical properties of ammonia, it follows that when dissolving ammonia to obtain 1 kg of an aqueous solution containing 34% by mass of ammonia, 598.8 kJ of heat is released. A calculated experiment determined that the thermal effect of the process of reducing pressure during the throttling of liquefied ammonia and evaporation of 0.34 kg of ammonia is -430.08 kJ. Thus, based on the heat balance equation of the installation, it follows that the amount of heat absorbed during the evaporation of liquid ammonia is not enough to absorb the heat of the ammonia dissolution reaction. However, if effect throttling and evaporation liquefied ammonia is used for cooling mixer - separator, in which will be to enter chilled low-concentration (20-24% mass) aqueous ammonia solution, then the amount released heat during

disammonia solution (for proof concentrations solution up to 34% by mass) on 1 kg solution will be 158.7 kJ. Considering thermal effect process throttling and evaporation liquefied of ammonia (430.08 kJ per 1 kg of the obtained aqueous solution) general heat loss will occur of the order of - 271.38 kJ per 1 kg of the solution, which is 4.44 kJ/(kg·K) heat capacity of the aqueous ammonia solution with a concentration of 34% by mass. It will allow it to cool down to 60 °C, more than enough for technological needs, obtaining an aqueous ammonia solution with high concentrations (not less than 34% by mass of ammonia).

Equilibrium pressure of saturated vapours over aqueous solution of ammonia (36 wt. %) as a function of temperature

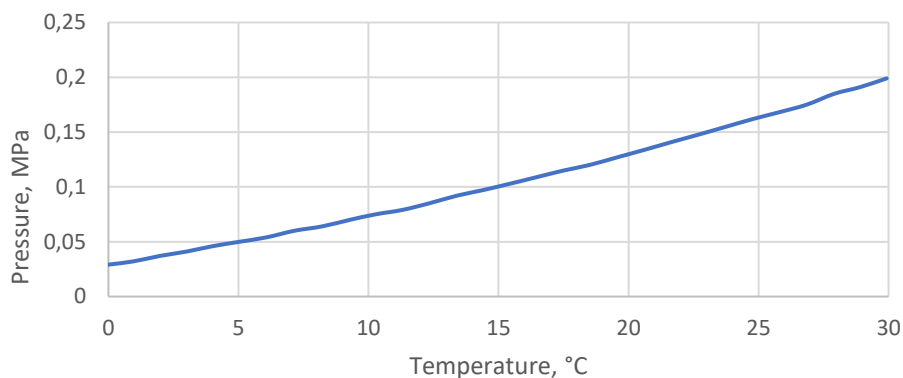


Fig. 4. Elasticity of liquefied ammonia vapour as a function of temperature.

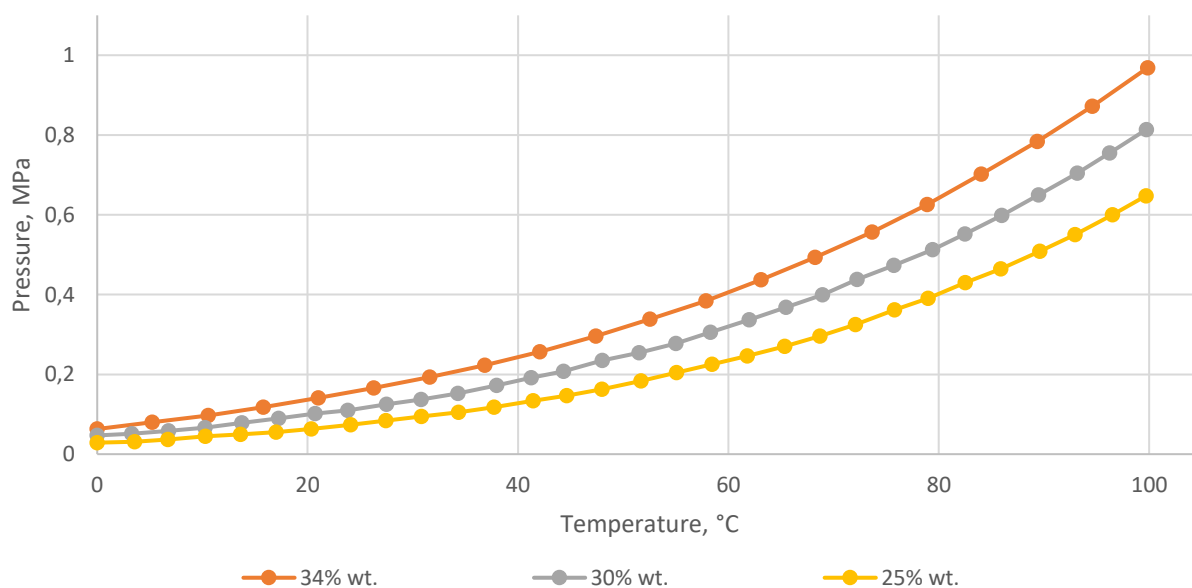


Fig. 5. Equilibrium pressure of saturated vapour over aqueous ammonia solution as a function of temperature.

However less, should note that thermodynamic parameters of such highly concentrated solutions (in terms of nitrogen not less than 32% by weight) during storage, transportation and application should be supported in the following within the limits: temperature below 5-6 °C (at atmospheric pressure), pressure (absolute) not lower than 0.2 MPa (when stored in a temperature range of up to 30 °C). Otherwise, dissolved ammonia will volatilize from ammonia water, which explains the decreased concentration.

Additionally, for the purpose of intensification of the technological process saturation of aqueous solution with gaseous ammonia, as well as to ensure uninterrupted work and promotion of safety level during operation of the main technological equipment installations, the following process-technological and hardware-design solutions are offered.

To reduce thermal loads on the absorption column, reduce temperatures contact temperature (absorption) and at the same time increase the solubility of ammonia in water to carry out:

- to implement not only cooling cube parts absorption columns, but also intermediate diversion absorbent from mass transfer sections for additional cooling (Fig. 6);
- to ensure stepped heat removal from each plate's mass transfer sections, replacing cap-shaped plates on contact elements with built-in heat exchange devices (Fig. 7);
- replace absorption column A-1 by two composite columns A-1 and A-2 with an intermediate cooling absorbent (Fig. 8), thereby having reduced the overall dimensions and weight of the installation unit are 2 times higher.

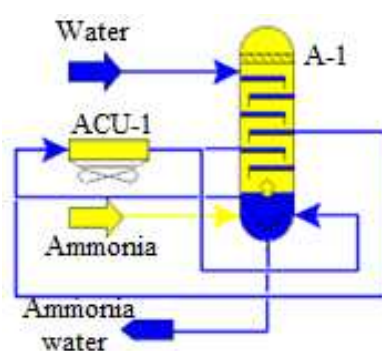


Fig. 6. Absorber with intermediate cooling absorbent.

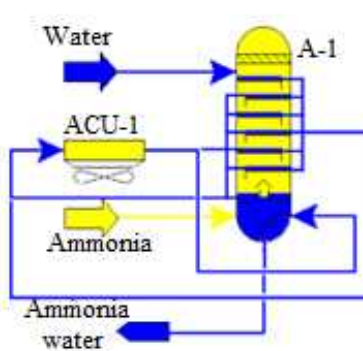


Fig. 7. Absorber with stepped heat removal from each plate.

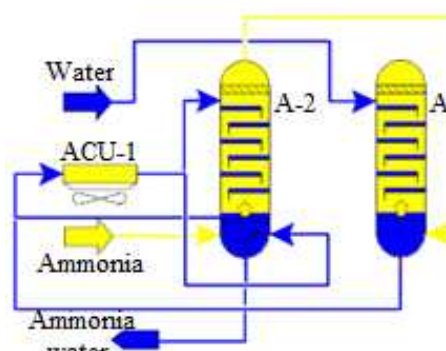


Fig. 8. Absorber from two composite absorption columns with intermediate cooling absorbent.

According to the proposed method in technology, the scheme does not provide for withdrawal gases from above absorption columns, which violates optimal hydrodynamic conditions, resulting in top plates that significantly reduce the intensity of process mass transfer at these stages. Under such conditions, the following are suggested:

- at the top parts absorption columns A-1 (in case of single-column installation) or in the entire A-1 column (in the case of two-column installation), replace the type of mass transfer contact elements from plate to packing (Fig. 9), which work more effectively at low gas loads phase;
- on the basis of the flow chart of Fig. 2 to provide recycling of gaseous ammonia from the top of the absorption column A-1 to the mixer-separator S-1, using the possibility of ejection by a high-speed gas flow passing through the throttling device (Fig. 10).

Consider the opportunity application of alternative hardware design at stages first and second steps of absorption (instead of absorption columns A-1 and (or) mixer-separator S-1, in particular, highly efficient combined heat and mass transfer devices (scientific developments departments, chemical engineering, Sumy State University):

- shell and tube gas-liquid reactor of volume-film type;
- vortex hollow absorber with rotating sprayer;
- vortex spraying counter-current mass transfer device.

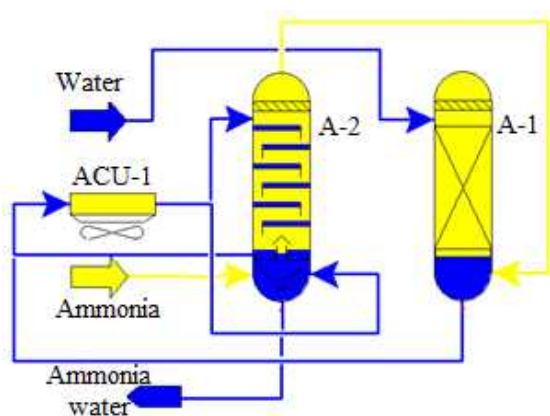


Fig. 9. Two-column absorption plant with two types of mass exchange contact elements (plates, nozzles).

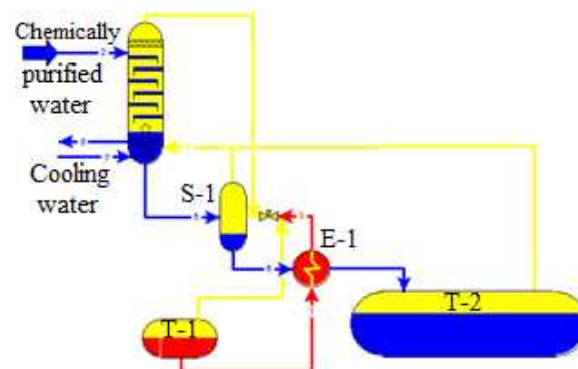


Fig. 10. Flow chart of the production of ammonia water at high concentrations.

Conclusions

The production of ammonia water by absorption of gaseous ammonia with water is a technological process that can be conditionally divided into two stages: dissolution of ammonia in water and removal of the heat released during the chemisorption process.

Ammonia is well soluble in water; therefore, the rate of the dissolution process and the technical characteristics of the technological equipment used for this (type, dimensions, etc.) are mainly determined by the slowest (limiting) stage of the process. For the technological process of dissolving ammonia in water, the limiting (least intensive) stage is the stage of removing the heat released in the process of obtaining ammonia water.

The use of bulk reactors with turbo-ejection mixing devices and various types of mixers, including cavitation type, designed to create a developed mass transfer surface between phases, will not generally increase the productivity of the production line and the efficiency of the main technological process.

Intensification of the stage of absorption of ammonia by water will lead to an increase in the rate of heat release and, accordingly, to an increase in the temperature of the phase contact. When the temperature exceeds some critical (equilibrium) values, the process of dissolving gaseous ammonia will stop, and the reverse process will begin - evaporation of gaseous ammonia from the surface of its aqueous solution.

Acknowledgements

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Interrelation of Quality Indicators of Coal Charge and Blast Furnace Coke

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Abstract. *The presented research is aimed at developing the scientific basis for the mechanism of bursting pressure, studying the influence of the nature of coal raw materials on the development of bursting pressure, and developing optimal technologies for preparing blends to improve the quality characteristics of coke. The possibility of predicting the composition of coal blends using the data on the properties of coal concentrates is shown.*

Keywords: charge, preparation, segregation, tamping, bursting pressure, compaction, mechanical strength, segregation.

Introduction

The need to produce high-quality metallurgical coke has led to the formation of a multi-basin raw material base at Ukrainian coke plants. To expand the raw material base of coking coal, it is necessary to introduce advanced technologies, such as modification of charges with additives, coking of rammed charges, and coking technology for thermally prepared charges. Inclusion of low-baking or non-baking coal in the composition of coal charges is possible with the introduction of partial briquetting of the charge.

The application of these methods directly affects the bulk density of the coal charge, sintering, and thus the quality of the coke produced and the production capacity of the coke chambers. However, all technological operations contribute to an increase in coking pressure (bursting pressure), which is an important criterion to consider when forming the composition of coal charges.

I Burst pressure

The influence of raw material factors of coal on the bursting pressure and properties of coke was studied [1]. 17 coal concentrates were used as the object of research: 6 are represented by the mark *gas*, 5 – mark *fatty*, 3 – mark *coking*, take one – mark long-flaming, gas fatty, and *lean caking*.

The study of the qualitative characteristics of coke was carried out using physical, mechanical, and thermochemical methods for the study of standardized indicators: crushability (M_{25}), abrasion (M_{10}), reactivity (CRI), and post-reaction strength (CSR). Mathematical statistics methods were used to analyze the influence of raw material and technological factors on the value of the bursting pressure.

The determination of the bursting pressure was carried out in a unified laboratory installation of the SE “UKHIN” (Fig. 1). The method consists in bilateral heating in a retort at a given temperature of the tested coal (charge) load of a certain mass and subsequent measurement of the bursting pressure using a piezoelectric pressure sensor in the range from 1 kPa to 70 kPa.

The correlation coefficients between the bursting pressure and the technological characteristics of coal charges were determined. The mathematical dependencies were obtained, and their statistical evaluation was carried out. The mechanism of influence of the bursting pressure on the strength characteristics of coke is confirmed. The possibility of predicting the composition of coal blends using the data on the properties of coal concentrates is shown.

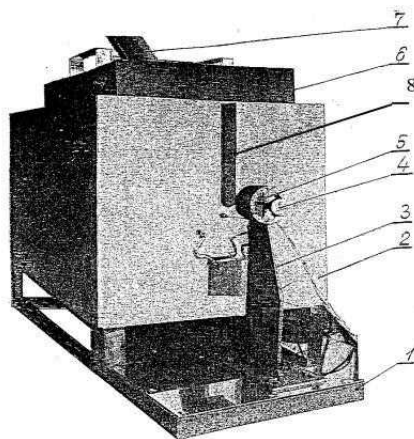


Fig. 1. Installation for determining the bursting pressure of coal and charge.

1 - base; 2 - electric furnace; 3 - bracket; 4 - adjusting screw; 5 - pressure sensor;
6 - heat-insulating cover; 7 - gas outlet pipe; 8 – hole.

Based on the study of the plastic-viscous properties of coal concentrates by the Giseler method, the connection between the peculiarities of the plastic state of coal of different degrees of metamorphism and the bursting pressure that it develops during coking was confirmed (Fig. 2).

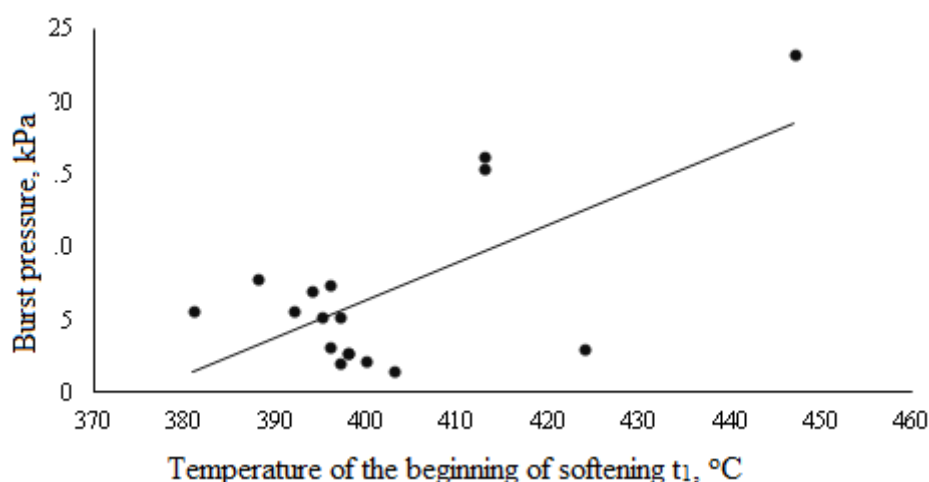


Fig. 2. Dependence of tensile pressure on the temperature of the beginning of coal softening.

The interrelation of the bursting pressure and the component composition of the coal mixture, the yield of volatile substances of the charge, and the petrographic characteristics (vitrinite content) was confirmed.

Based on the processing of experimental data using the methods of mathematical statistics, regression equations were obtained that make it possible to predict the bursting pressure and optimize the composition of coal blends, which will allow controlling the indicator during re-blending and reducing the number of experimental measurements of bursting pressure in the conditions of a particular coke production [2].

The mechanism of influence of the bursting pressure on the strength characteristics of coke has been confirmed. Thus, an increase in the bursting pressure causes an increase in the amount of liquid products, deepening their interaction with softened coal grains, which improves the sinterability and coking properties of the charge and, as a result, increases the mechanical strength of coke [3].

The work of tamping, which must be applied to achieve the required density and stability of the coal cake, is investigated. The proportional dependencies of the tamping operation and the technological parameters and characteristics of coal charges were established. The tamping tests were carried out at the installation of SE “UKHIN” (Fig. 3).

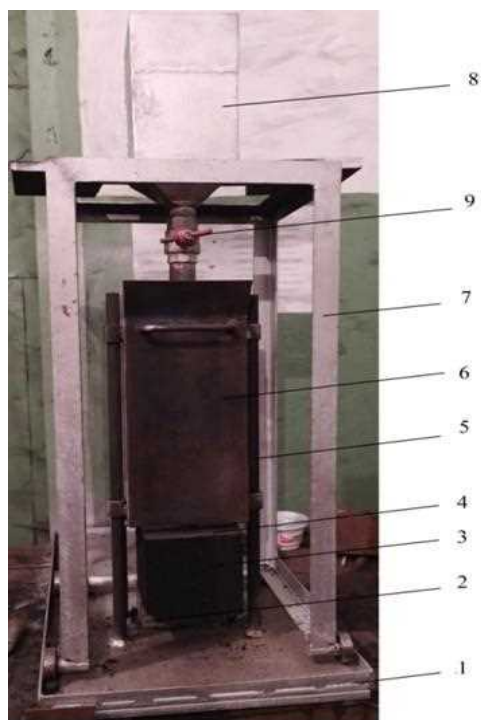


Fig. 3 Device for determining the shear strength of a rammed cake: 1 - base, 2 - table, 3 - test sample (briquette), 4 - metal plate, 5 - container guide, 6 - container, 7 - mobile hopper device, 8 - hopper with a fraction of lead, 9 - on/off valve.

The prepared charges were cooked in a 5-kg laboratory furnace developed by UHIN SE. The coke was quenched by drying. The coke was weighed, and the gross dry coke yield was determined from the dry coal loading.

The resulting coke was subjected to destructive forces to reveal cracks by dropping it 4 times from a height of 1 m on a metal plate, after which the coke was sieved (calibrated) on sieves with round holes with diameters of 70, 60, 50, 40, 25, and 10 mm. The sieving results were used to calculate the yield of individual size classes.

II Coal segregation

The paper investigates the process of coal segregation in a real industrial coke plant, both in terms of size and the main parameters of coal quality [4]. The object of research was coal concentrates, which are part of the raw material base Coal Preparation Department-2 PJSC «Avdiivka Coke Oven Plant». Batch composition: 4 gas, 4 fatty, 3 coking, and 1 lean caking coal. The submitted samples of coal concentrates were analyzed by a set of standardized methods to determine the data of technical, petrographic, and particle size analysis, including determination of ash content, volatile matter yield of the obtained size classes, as well as the Hardgrove grindability coefficient and Horne index.

The study was carried out at PJSC «Avdiivka Coke Oven Plant», respectively, the injection, initial selection and analysis of the distribution of the charge were carried out in relation to the two-section coal tower built at this enterprise with a stationary reversible conveyor and charge distribution chutes, where the distribution of the charge into sections is carried out by a stationary reversible belt conveyor with valves (Fig. 4).

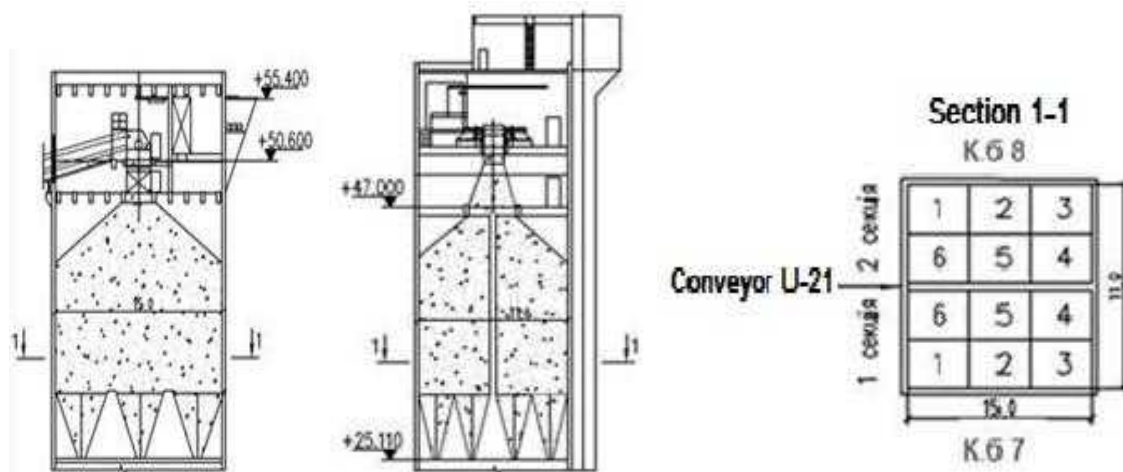


Fig. 4. Coal tower with charge chutes and valves.

According to the results of this study, the ash content by coal size class is unevenly distributed; excessive grinding of coal with the formation of an increased number of classes less than 0.5 mm can lead to “self-lean caking” of the charge and, accordingly, deterioration of its quality. It is possible to state the relative stability of the technological properties and particle size distribution of the coal charge during its injection into the coal tower.

Conclusions

With an increase in the content of low-stage metamorphism coal in the charge from 37 to 49% and a decrease in the content of high-stage metamorphism coal from 57 to 45%, a gradual decrease in the compaction of the charge from 22.5 to 21.1 kPa, an increase in the bursting pressure from 6.8 to 5.9 kPa, as well as tamping work to achieve the specified density of the coal cake of 1.15 t/m³ per wet state of the charge from 8966 to 6822 J is observed.

The work and/or tamping time is inversely proportional to the content of low-stage coal in the charge, the content of the sum of fusinized components of the charge ΣFC and the content of volatile substances in the charge V^{daf} , while it is directly proportional to the average arbitrary reflectance of the vitrinite of the charge R_0 and the vitrinite content V_t .

An increase in the content of low-stage metamorphism coal in the blends leads to a decrease in the quality of the coke obtained from them. The mechanical strength of the studied cokes was close (91.0 - 91.5%), and the abrasion of cokes decreased from 7.3% to 7.8 and 8.0%.

The expediency of introducing technological measures to eliminate segregation and equalize the quality of the charge was shown, which should lead to stabilization of the quality of blast furnace coke produced at the enterprise.

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Development and Optimization of Lithium Aluminosilicate Glass-Ceramic Materials with High β -Spodumene Content for Armor Protection

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Abstract. *This paper presents lithium aluminosilicate glass-ceramics with up to 80% β -spodumene developed using optimized compositions and a two-stage heat treatment. The materials exhibit high hardness (8.5–9.0 GPa), optimal elasticity (318–324 GPa), fracture toughness (8.0–8.4 MPa·m^{0.5}), and low density (2400–2420 kg/m³), making them promising for lightweight armor.*

Keywords: lithium aluminosilicate, glass-ceramic material, armor protection, β -spodumene, two-stage heat treatment, catalysts, modifying components, impact resistance, optimization.

Introduction

Modern defense and security challenges require materials that combine high mechanical strength, impact resistance, and low weight. Traditional armor ceramic systems, particularly those based on SiC, exhibit high hardness; however, their high production cost and limited capacity to absorb impact energy [1], [2] restrict their use in mobile systems. Spallitized lithium aluminosilicate glass-ceramic materials are a promising solution, as they contain over 80% β -spodumene due to the formation of a fine-dispersed crystalline structure that effectively dissipates impact energy.

This work is aimed at optimizing compositions, heat treatment regimes, and the use of catalysts and modifying components to obtain materials with superior performance characteristics that can be integrated into the production of lightweight armor protection systems.

Methodology

In this study, a series of experimental glass compositions (Series SP) based on the system $R_2O-RO-RO_2-R_2O_3-Li_2O-CaO-P_2O_5-SiO_2$ was developed.

The main idea was to form up to 80% of the β -spodumene phase through optimization of the chemical composition and heat treatment regimes. The methodology comprises the following stages:

- Selection of primary components: the use of SiO_2 , Li_2O , and Al_2O_3 ensures the formation of a basic matrix in which β -spodumene will develop;
- Addition of modifying components: incorporating modifying agents (Na_2O+K_2O , B_2O_3 , $CaO+MgO+ZnO$) and fluorides (LiF , CaF_2) enables the adjustment of the melting temperature and viscosity of the melt, thereby influencing the crystallization behavior;
- One-stage heat treatment: heating the material in the temperature range of 450–950 °C for 6 hours achieves overall crystallization; however, this approach may leave residual internal stresses (Table 1);
- Two-stage heat treatment: first stage (450–650 °C, 4 hours) stimulates the formation of nucleation centers, second stage (700–950 °C, 4 hours) promotes crystal growth, resulting in a fine-dispersed, homogeneous structure with minimal residual stresses (Table 1);

- Application of catalysts: the addition of TiO_2 , ZrO_2 , and SnO_2 ensures an even distribution of crystalline nuclei and promotes fine-dispersed crystallization, which is critical for enhancing the mechanical properties;
- Characterization: hardness, modulus of elasticity, fracture toughness, and density were determined and are presented in Figs. 1–4.

During the study, it was determined that the optimized compositions of the SP series form a fine-dispersed crystalline structure with a high content of β -spodumene (over 80%).

The uniform distribution of crystals was achieved using a two-stage heat treatment process, which reduces residual stresses as confirmed by X-ray diffraction and scanning electron microscopy.

Testing showed that the obtained materials exhibit high mechanical properties, as presented in Figs. 1–4.

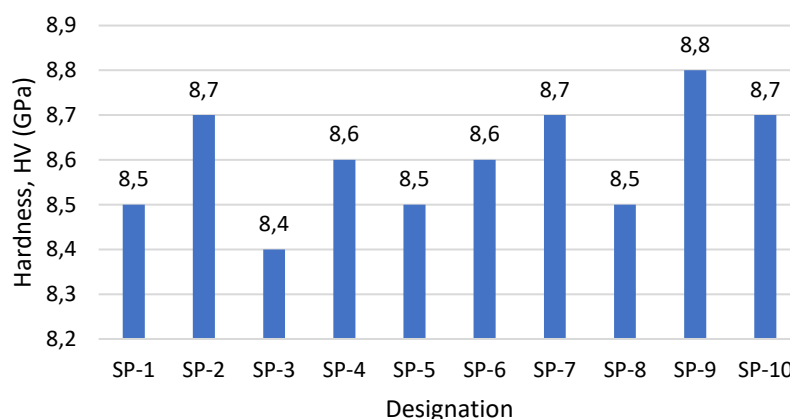


Fig. 1. Hardness, HV (GPa).

The graph (Fig. 1) shows that the hardness (HV) values for the experimental compositions range from 8.4 to 8.8 GPa, indicating the material's stable resistance to local deformation.

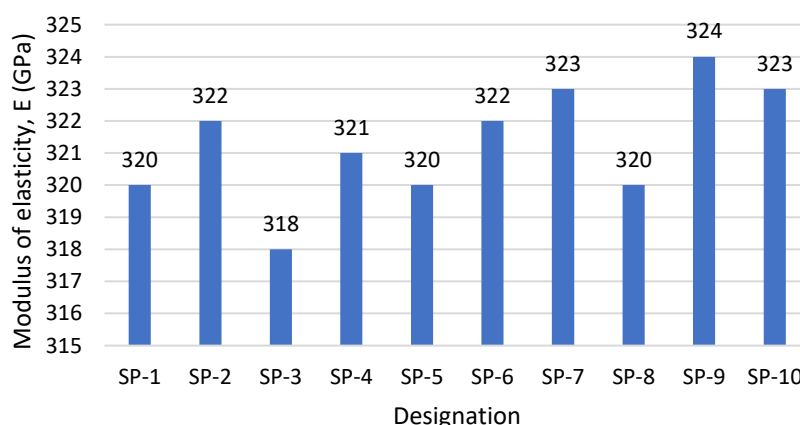
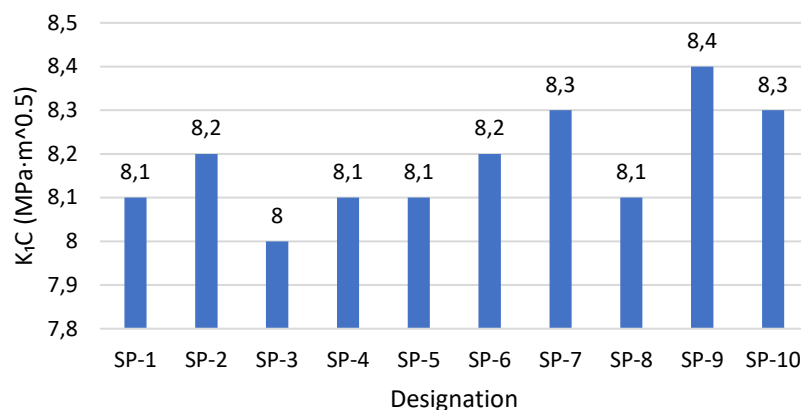
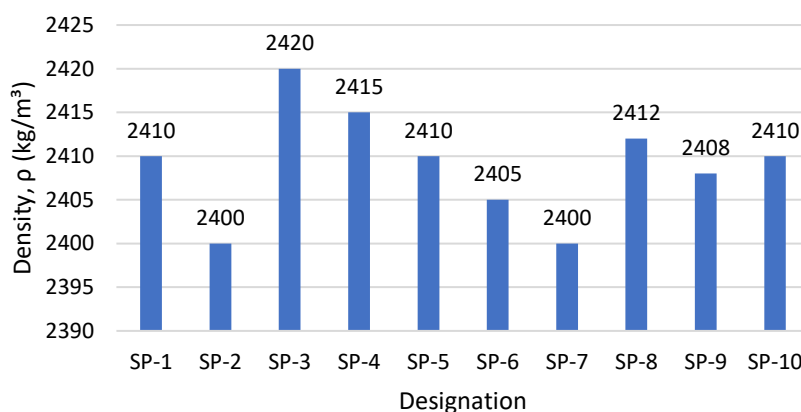


Fig.2. Modulus of elasticity, E (GPa).

The graph (Fig. 2) illustrates that the modulus of elasticity (E) is in the range of 318–324 GPa, ensuring an effective distribution of impact energy.

The graph (Fig. 3) demonstrates that the fracture toughness (K_{IC}) values are between 8.0 and $8.4 \text{ MPa} \cdot \text{m}^{0.5}$, which is critical for preventing the propagation of cracks.

The graph (Fig. 4) shows that the density of the materials ranges from 2400 to 2420 kg/m^3 , enabling the production of lightweight armor protection products.

Fig. 3. K₁C (MPa·m^{0.5}).Fig. 4. Density, ρ (kg/m³).

Comparison of the one-stage and two-stage heat treatment regimes (Table 1) revealed that the two-stage process provides a more uniform fine-dispersed structure with lower residual stresses, which positively affects the material's mechanical properties.

Table 1

Comparison of heat treatment regimes

Heat treatment regime	Temperature range (°C)	Heat treatment time (hours)	Main results	Advantages / disadvantages
One-stage	450 – 950	6	Uniform crystallization with some residual stresses	Simplicity of the process, lower energy consumption; less precise control over crystal size
Two-stage	1st stage: 450–650 2nd stage: 700–950	4 + 4	Fine-dispersed, homogeneous crystalline structure, minimal residual stresses	Higher mechanical strength, improved impact resistance; more complex process, higher energy consumption

From Table 1, it is evident that the two-stage heat treatment provides significantly better control over the material's structure: the formation of a fine-dispersed crystalline structure contributes to increased hardness, modulus of elasticity, and fracture toughness. The comparison of regimes justifies the choice of a more complex but more effective technological process to achieve optimal material properties.

Discussion

The obtained results indicate that the optimization of compositions and the application of a two-stage heat treatment are key factors in achieving high impact resistance of lithium aluminosilicate glass-ceramic materials.

The uniform distribution of the crystalline phase, ensured by the use of crystallization catalysts (TiO_2 , ZrO_2 , SnO_2) and a two-stage heat treatment, allows for effective dissipation of impact energy. This reduces the risk of microcrack formation and propagation, which is critical for armor applications.

High values of hardness and modulus of elasticity indicate the material's ability to withstand deformation and absorb impact energy. In addition, the low density enables the production of lightweight structures, which is essential for the mobility of protective equipment.

Comparison of the heat treatment regimes shows that, despite higher energy consumption, the two-stage heat treatment yields a more optimal structure. This is confirmed by the data presented in Table 1 and the corresponding Figs. 1–4, which demonstrate improvements in the mechanical properties of materials processed by this regime.

The study results confirm that the developed materials have potential for use in the production of body armor, helmets, and armored vehicle components [3-5], as they combine high mechanical properties with low weight. Further optimization of the technological process and scaling up production will allow these materials to be implemented in practical defense solutions.

Conclusions

In conclusion, the conducted research demonstrates that the optimization of lithium aluminosilicate glass-ceramic compositions through the use of a two-stage heat treatment, crystallization catalysts, and modifying components enables the production of materials with high hardness, impact resistance, and reduced density. These characteristics make them promising for the production of lightweight armor protection systems that meet modern requirements for mobility and effective protection. Further research should focus on further optimization of the technological process, reduction of energy consumption, and scaling up production for practical application in the defense industry.

Acknowledgments

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Kinetics of Filtration Drying of Wild Carrot Pomace

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Abstract. *The study presents the results of research on the kinetics of filtration drying of wild carrot pomace for the production of alternative solid fuel. The relevance of choosing this material as the research object is justified. The influence of the height of the stationary layer, the temperature of the heating agent, and its filtration rate through the stationary layer of wild carrot pomace on the drying process is analyzed. A graphical dependence of the filtration drying rate on the material's current moisture content is provided, along with an investigation of the moisture removal dynamics and drying rate under different heating agent parameters and stationary layer heights.*

Keywords: kinetics, filtration drying, hydrodynamics, stationary layer, wild carrot pomace.

Introduction

A significant portion of plant waste in Ukraine comes from the pharmaceutical industry. One such waste product is wild carrot pomace, which is formed as a byproduct of extracting target components from the plant. In many cases, this plant waste is disposed of by transporting it to landfills. During the decomposition process, harmful leachate is released, which negatively impacts the environment. Therefore, the issue of waste utilization or recycling is highly relevant. One potential method of utilizing wild carrot pomace is through the production of fuel briquettes, which are an alternative, eco-friendly solid fuel. The production process for biomass fuel briquettes involves drying the material to a moisture content not exceeding 14% by mass [1]. This not only extends the shelf life of the biomass as raw material but also enhances the quality of the resulting alternative fuel.

Filtration drying was chosen as the method for drying wild carrot pomace because it is highly efficient for drying finely ground plant materials in a stationary layer. The kinetics of filtration drying have been studied by several researchers. For example, in [2], researchers investigated the kinetics of filtration drying of barley brewing spent grain. In [3], the authors examined the kinetics of filtration drying of corn distillery stillage. These studies demonstrated the influence of different layers and heating agent parameters on the drying intensity. The kinetics of filtration drying of veneer shavings was investigated in [4].

However, the results of these studies cannot be directly applied to the stationary layer of wild carrot pomace due to differences in material properties. Each material exhibits unique characteristics, such as layer porosity, the equivalent diameter of the channels between particles, and fractional composition.

Experimental part

The study of the kinetics of filtration drying of wild carrot pomace, the dynamics of moisture removal, and the drying rate as a function of the current moisture content was carried out using the experimental setup described in [5]. The initial moisture content of the material was 41.5%. Experiments were carried out under various heating agent parameters: temperatures (40, 50, 60, 70, 80 °C), flow velocities (1.2, 1.7, 2.2, 2.6, 3.1 m/s), and different stationary layer heights of wild carrot pomace (40, 60, 80, 100 mm). Filtration drying was conducted until the material reached a moisture content of 5%.



Fig. 1. Wild carrot pomace particle under a microscope, MBB-1A model.

Results and discussion

The results of the investigation into the effect of the heating agent filtration rate through the stationary layer of wild carrot pomace on drying time are shown in Fig. 2a. Fig. 2b illustrates the dynamics of moisture removal from the material, while Fig. 2c presents the dependence of the drying rate on the moisture content of wild carrot pomace. The temperature of the heating agent was 60 °C, and the stationary layer height was 80 mm.

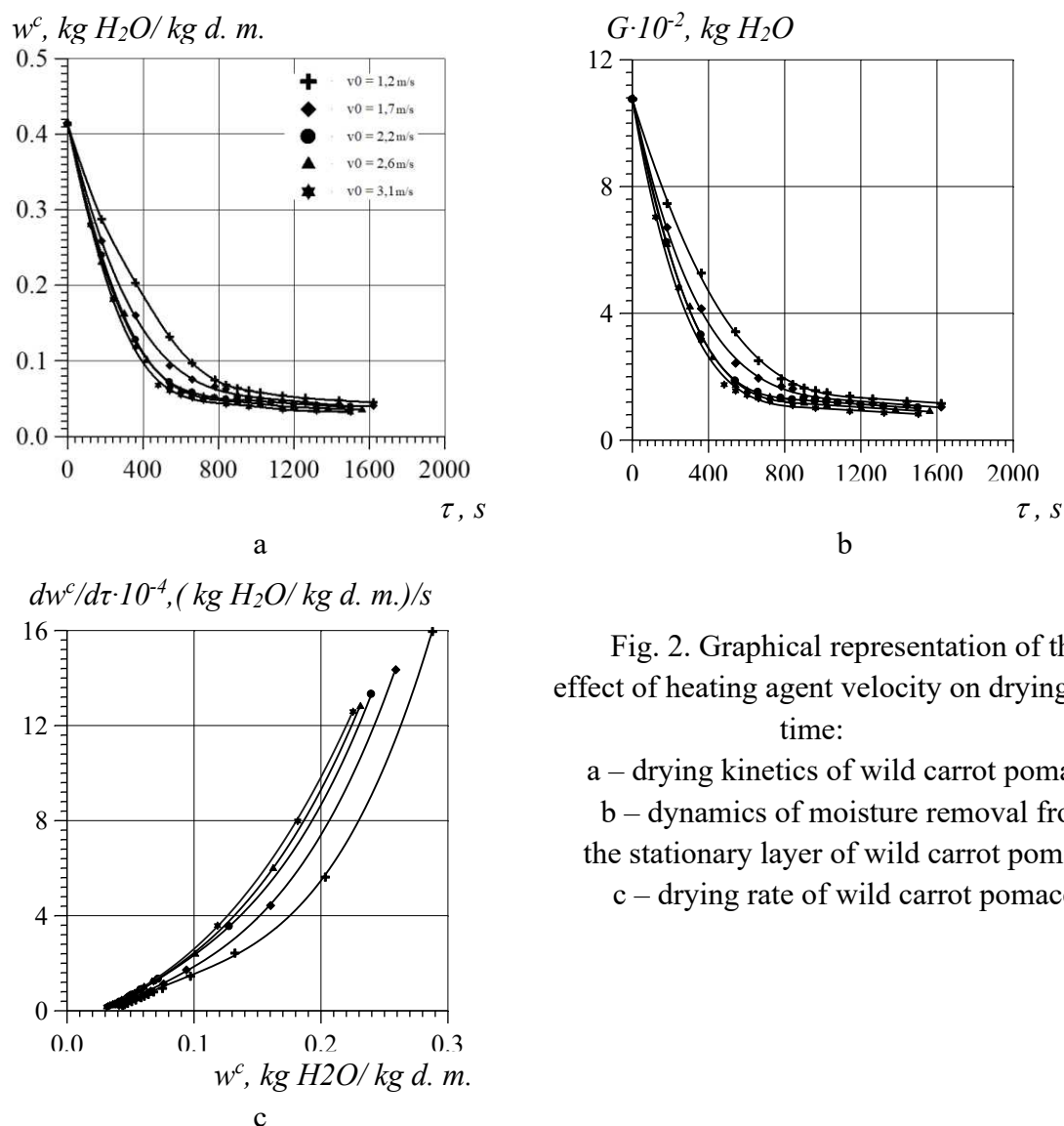


Fig. 2. Graphical representation of the effect of heating agent velocity on drying time:

- a – drying kinetics of wild carrot pomace;
- b – dynamics of moisture removal from the stationary layer of wild carrot pomace;
- c – drying rate of wild carrot pomace.

Fig. 3 presents the results of the study on the kinetics of filtration drying of wild carrot pomace at different heating agent temperatures, with a filtration rate of 2.2 m/s and a stationary layer height of 80 mm.

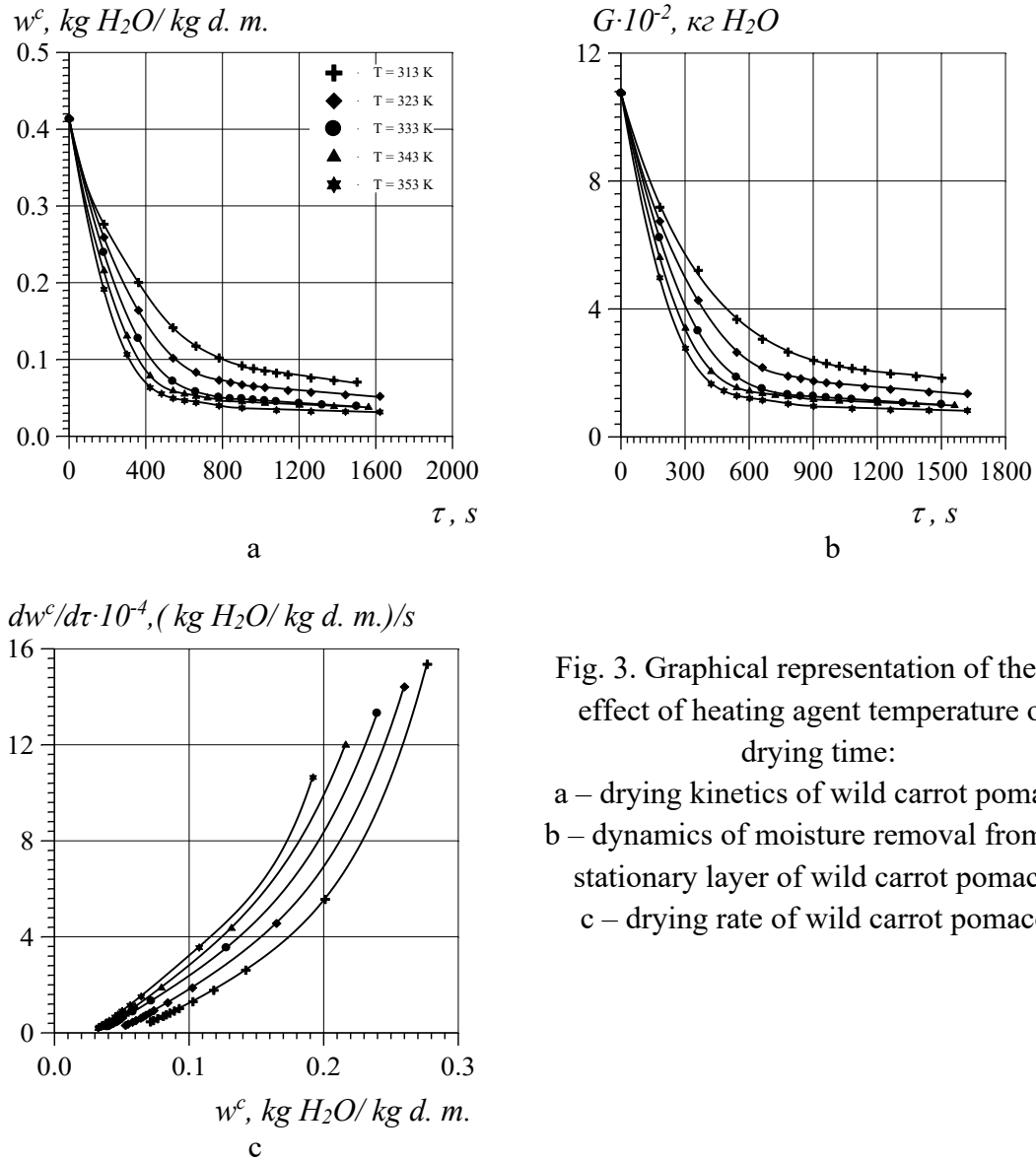
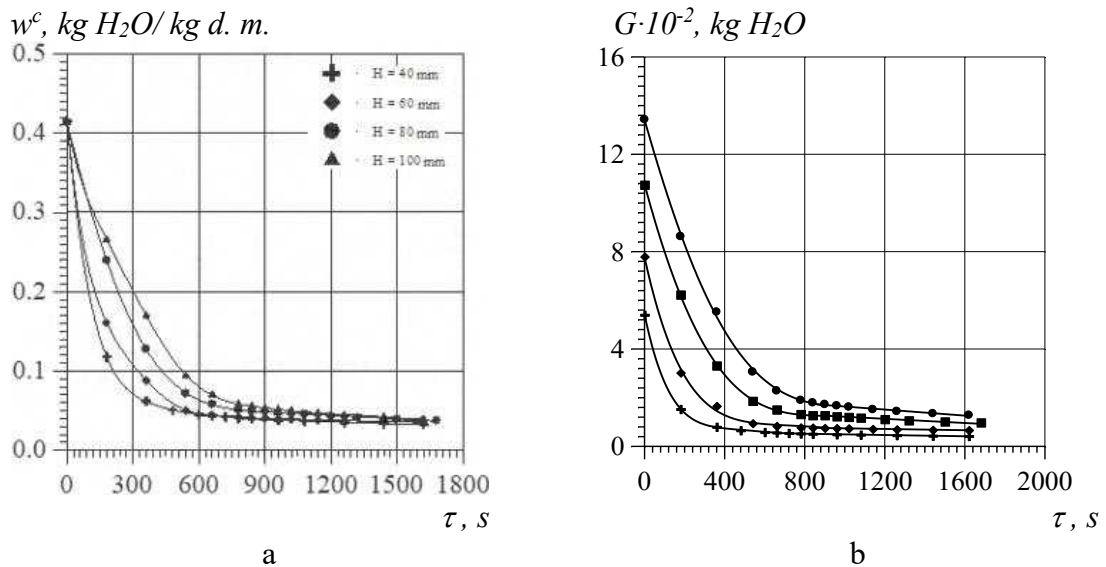


Fig. 3. Graphical representation of the effect of heating agent temperature on drying time:
 a – drying kinetics of wild carrot pomace;
 b – dynamics of moisture removal from the stationary layer of wild carrot pomace;
 c – drying rate of wild carrot pomace.

By analyzing Figs. 2a and 3a, it can be concluded that an increase in the velocity and temperature of the heating agent leads to a higher drying intensity.



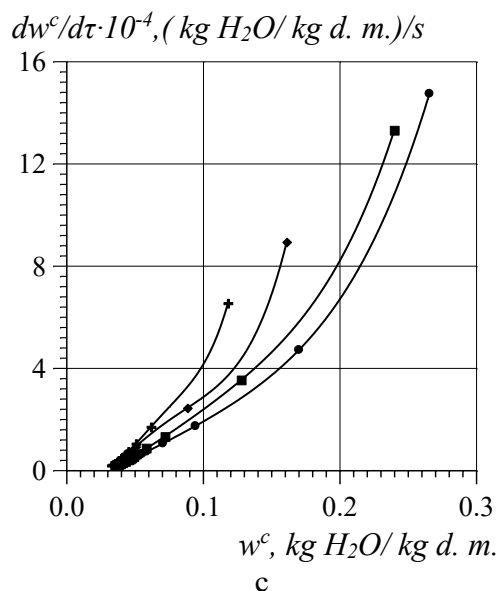


Fig. 4. Graphical representation of the effect of stationary layer height on drying time:

- a – drying kinetics of wild carrot pomace;
- b – dynamics of moisture removal from the stationary layer of wild carrot pomace;
- c – drying rate of wild carrot pomace.

Fig. 4 shows the results of the study on the kinetics of filtration drying of wild carrot pomace at different stationary layer heights. The temperature of the heating agent was 60 °C, and its velocity through the stationary layer was 2.2 m/s. As shown in Fig. 4a, as the height of the stationary layer of wild carrot pomace increases, the tangent of the slope of the curve decreases. This indicates that the path for the mass transfer front becomes longer.

Based on the results of the study, the optimal drying parameters for wild carrot pomace were determined as follows: $H = 80$ mm; $v_0 = 2.2$ m/s; $T = 333$ K.

Conclusions

The study investigated the kinetics of filtration drying of wild carrot pomace. Specifically, the experimental impact of parameters such as temperature, heating agent velocity through the stationary layer of wild carrot pomace, and the height of the stationary layer on the drying rate was determined. The optimal drying parameters for wild carrot pomace were identified.

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Development of Bio-Based Epoxy Thermosetting Materials Based on Imine Bonds

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Abstract. *Bio-based epoxy thermoset materials were synthesized using lignin-derived vanillin and syringaldehyde, along with naringenin, a non-toxic flavonoid. Schiff bases were polymerized via self-polymerization, initiator-assisted, and TGEN-copolymerization strategies. These materials exhibited high glass transition values, $T_g \sim 138\text{--}249\text{ }^\circ\text{C}$, recyclability, and flame resistance (LOI 33–37%), offering sustainable alternatives for advanced materials applications.*

Keywords: Bio-based epoxy, Schiff base, imine linkages, naringenin, thermal stability, recyclability, flame resistance, sustainable polymers, vanillin, syringaldehyde.

Introduction

Epoxy thermoset resins are widely used across various industries due to their unique mechanical properties and versatility. However, the use of bisphenol A (BPA) as a key building block raises significant environmental and toxicological concerns. BPA has been classified as an endocrine disruptor and a chemical potentially impairing reproductive function, leading to stricter regulations on its use. Moreover, cured epoxy resins form rigid three-dimensional networks, making them difficult to recycle and contributing to waste accumulation [1].

To address these challenges, developing epoxy resins from non-toxic and renewable sources has become a crucial task. One promising solution is the use of lignin, a by-product of the pulp and paper industry. Lignin can be processed into aromatic compounds such as vanillin and syringaldehyde, which can serve as precursors for bio-based polymers. In this study, vanillin (VAN) and syringaldehyde (SYR) reacted with p-phenylenediamine (DiAP) and p-aminophenol (AP) to form Schiff based monomers: EP-VAN-DiAP, EP-VAN-AP, EP-SYR-DiAP, and EP-SYR-AP [2].

Materials and Testing

Considering the environmental challenges, the development of epoxy resins from non-toxic and renewable sources is an urgent task. One promising solution is the use of lignin, a byproduct of the pulp and paper industry. Lignin can be processed into aromatic compounds such as vanillin and syringaldehyde, which can be used to create bio-based polymers. In this study, vanillin (VAN) and syringaldehyde (SYR) were reacted with p-phenylenediamine (DiAP) and p-aminophenol (AP) to form four Schiff based epoxy monomers: EP-VAN-DiAP, EP-VAN-AP, EP-SYR-DiAP,

and EP-SYR-AP (Fig. 1). The synthesis of the epoxy monomer involved two stages. In the first stage, phenolic groups were converted into epoxy groups through a reaction with epichlorohydrin in the presence of a phase transfer catalyst (TEBAB). The reaction proceeded solvent-free, adhering to the principles of green chemistry. In the second stage, the epoxy cycles were closed in an alkaline medium using an aqueous sodium hydroxide solution [2, 3].

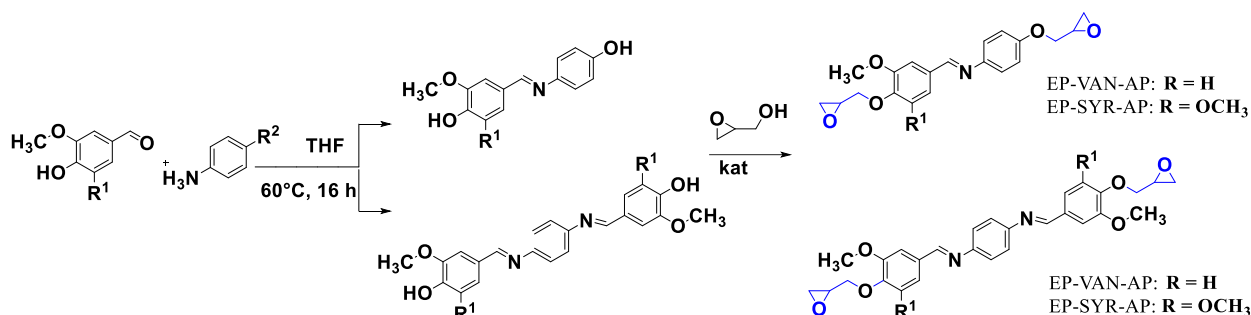


Fig. 1. Scheme of synthesis of epoxidized Schiff bases: EP-VAN-DiAP, EP-VAN-AP, EP-SYR-DiAP, and EP-SYR-AP.

Optimization of these parameters resulted in yields ~ 72 -80% of diglycidyl monomers, including triglycidyl ether of naringenin (TGEN, Fig. 2), with yields of 96-98%, which was synthesized similarly. Naringenin, a natural flavonoid, is non-toxic and biologically safe, making it an ideal candidate for developing sustainable polymers. The green metrics, such as E-factor (EF) and simple E-factor (sEF), were calculated for all synthesized monomers [3].

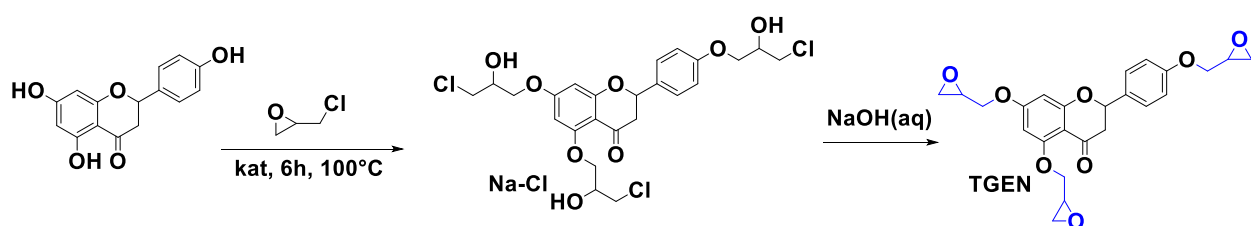


Fig. 2. Scheme of synthesis of TGEN.

The diglycidyl Schiff based monomers were tested using three strategies: self-polymerization, polymerization with the addition of an initiator (1-methylimidazole), and copolymerization with TGEN. Schiff-based monomers can self-polymerize without curing agents or catalysts due to their unique structure. Their nucleophilic sp^2 -hybridized nitrogen readily attacks the epoxide ring, initiating polymerization and forming a stabilized intermediate. While the π - π stacking initially slows the reaction, elevated temperatures cause a conformational shift that reduces steric hindrance and increases reactivity, allowing imidazole-like polymerization (Fig. 3). The addition of an initiator reduced the onset temperature (T_{onset}) and increased network uniformity. The introduction of TGEN enhanced the rigidity and thermal stability of the resulting materials but reduced their susceptibility to chemical recyclability [2, 3].

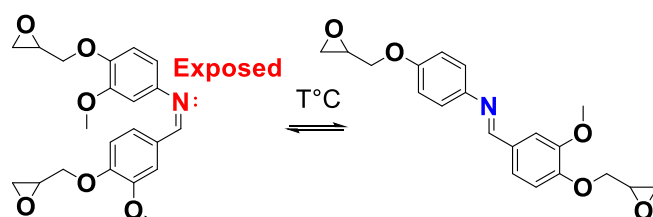


Fig. 3. The structure of EP-VAN-AP in cis and trans isomerization.

Differential scanning calorimetry (DSC) provided valuable insights into the thermal behavior of the synthesized materials, which was expected given the high degree of crosslinking

confirmed by the gel content analysis (GC,%). The glass transition values (T_g) of the self-polymerized Schiff-based monomers ranged from 134 to 214 °C, whereas the polymerization of DGEBA without an initiator did not occur at all. The addition of the initiator, 1-methylimidazole, significantly increased the T_g values, in the range 112–290 °C. The incorporation of TGEN notably enhanced the rigidity of the resulting polymer networks, leading to T_g values~ 174–224 °C, which is considerably higher than that of the DGEBA mixture (84 °C). Table 1 presents the data on T_g , T_α , and GC%, providing a clear comparison with the results obtained for DGEBA based thermosets.

Table 1

Thermo-mechanical properties of the designed thermosets

Samples	T_g [°C]	T_α [°C]	GC [%]	Samples	T_g [°C]	T_α [°C]	GC [%]
DGEBA	-	-	-	DGEBA + 1MIM	65	122	95.93
EP-VAN-DiAP	214	219	99.73	EP-VAN-DiAP + 1MIM	209	220	99.56
EP-VAN-AP	130	138	99.61	EP-VAN-AP + 1MIM	119	186	98.89
EP-SYR-DiAP	183	217	98.69	EP-SYR-DiAP + 1MIM	177	215	98.44
EP-SYR-AP	134	144	99.95	EP-SYR-AP + 1MIM	112	201	99.95
Samples				T_g [°C]	T_α [°C]	GC [%]	
DGEBA/TGEN + 1MIM				84	119	99.89	
EP-VAN-DiAP/TGEN + 1MIM				224	249	98.65	
EP-VAN-AP/TGEN + 1MIM				189	241	98.94	
EP-SYR-DiAP/TGEN + 1MIM				213	243	98.68	
EP-SYR-AP/TGEN + 1MIM				174	194	99.56	

The storage E' modulus varied between 0.96 and 2.16 GPa at 25 °C, depending on the composition. TGA analysis demonstrated excellent thermal stability across all Schiff-based systems, with decomposition temperatures at 5% weight loss ($T_5\%$) ranging from 310 to 350 °C in an oxidizing atmosphere and from 270 to 330 °C in an inert atmosphere. After decomposition, the residual carbon content reached up to 49%, providing Schiff-based materials with superior fire resistance compared to DGEBA. The limiting oxygen index (LOI), which indicates fire resistance, ranged from 33% to 37%.

To assess recyclability, the materials were exposed to acidic solutions (0.2 M HCl and H_2SO_4) at 50 °C. In systems without TGEN (e.g., EP-SYR-DiAP), degradation was completed within 10 hours, whereas copolymers with TGEN remained stable for more than a week. This is attributed to the high rigidity of the triglycidyl structure, which prevents network breakdown. A stronger acid (HCl) facilitated faster degradation due to the high concentration of protons initiating the hydrolysis of imine bonds.

Hot compression molding (Fig. 4) was used to reprocess crosslinked samples by crushing them into small pieces and heating under 15 MPa pressure for 2 hours at $T_g + 40$ °C. This process successfully restored the bio-based thermosets, leveraging the reversible nature of imine bonds through transamination reactions. The rigidity of the polymer backbone required high temperatures to facilitate bond exchange, effectively recombining polymer fragments. Additionally, π - π stacking interactions contributed to network restoration [2, 3].

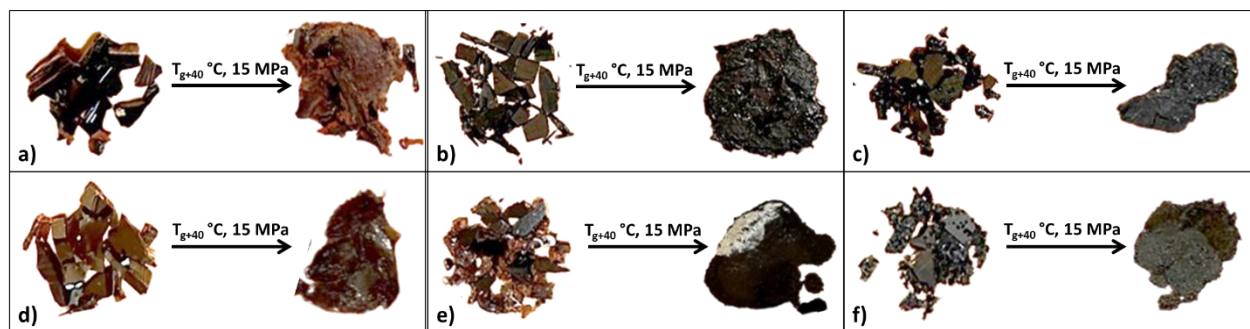


Fig. 4. Physical appearance of the grinded and thermally reformed samples: a) EP-SYR-AP; b) EP-SYR-AP+1MIM; c) EP-SYR-AP/TGEN+1MIM; d) EP-VAN-AP; e) EP-VAN-AP+1MIM; f) EP-VAN-AP/TGEN+1MIM.

Table 2 compares the thermo-mechanical properties of virgin and reprocessed EP-VAN-AP thermosets. The reprocessed samples showed a higher T_α (146 °C vs. 138 °C), reduced $\tan \delta$ peak amplitude, and a drop in storage modulus (E') from 1.80 GPa to 0.67 GPa at 25 °C. These changes suggest increased crosslinking and reduced chain mobility, resulting in a more rigid network. However, the decreased storage modulus indicates potential structural defects, such as microvoids, affecting stiffness.

Table 2

Thermomechanical properties (by DMA and DSC) of the virgin and reprocessed EP-VAN-AP thermosets

Samples	T_{g-DSC} [°C]	T_α [°C]	$\tan \delta$	E' at 25 °C [GPa]
EP-VAN-AP_virgin	130	138	0.76	1.80
EP-VAN-AP_recycled	139	146	0.43	0.67

Conclusions

We have successfully obtained epoxidized monomers and thermosets from natural and renewable building blocks. The proposed bio-based epoxy thermosets demonstrate excellent thermal stability, mechanical strength, flame retardancy, and recyclability. These properties make them highly promising for applications in high-tech industries such as aerospace, automotive, and construction. The developed approaches pave the way for the creation of environmentally friendly, high-performance polymers with outstanding thermomechanical properties. given.

Acknowledgments

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Research on a Combined System with a Hybrid Solar Collector

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Abstract. *The authors have developed a model of a system with a hybrid solar collector that can simultaneously produce thermal and electrical energy. The dependencies of heat transfer fluid temperature changes in the hybrid thermal photovoltaic solar collector on its solar radiation exposure time were obtained, and the patterns of their changes over time were characterized. Additionally, the temperature change of the heat transfer fluid in the thermal storage tank was studied.*

Keywords: energy supply, solar collector, alternative energy sources, heat supply.

Introduction

The rising cost of traditional energy sources, competition for their deposits, wars, and environmental pollution - all drive the increasing use of non-traditional energy sources. Therefore, improving existing systems and developing new ones capable of harnessing energy from alternative sources is currently relevant. The main objective of this research is to develop an improved hybrid thermal photovoltaic solar collector and study its thermophysical characteristics through modeling.

Materials and Research Methods

The model of the proposed hybrid solar collector consisted of two parts: thermal and photovoltaic, with silicon photocells. The heat transfer fluid pipelines were made of copper, and the concentrators of the thermal part were made of polished aluminum in a parabolic shape. The thermal storage tank was made of steel and contains a copper heat exchanger.

Mathematical methods for planning a multi-factor experiment and processing its data were implemented using the SolidWorks software package for modeling and research.

The obtained results do not contradict the conclusions of known scientific principles. The conclusions and recommendations formulated as a result of these studies were confirmed through analysis, generalization, and systematization.

Research Results

The combined energy supply system with a hybrid thermal photovoltaic solar collector without protective glass and a heat exchanger in the thermal storage tank is shown in Figure 1. The following symbols are used in the figure: 1, 4 - pipelines at the inlet and outlet of HTFPC; 2, 7 - heat transfer fluid distribution manifolds at the inlet to the photovoltaic panel and at the outlet of the thermal solar collector; 3 - thermal storage tank; 5 - photovoltaic panel; 6 – heat exchanger.

The model of the developed CESHP with HTFPC construction consists of two separate blocks - thermal storage tank 8 and HTFPC, which includes a photovoltaic panel and thermal solar collector, and is designed to produce thermal and electrical energy. The incident solar radiation on the thermal solar collector is focused in seven concentrators, which are adjacent aluminum parabolic-shaped plates that concentrate the solar rays reflected from their walls onto copper tubes 21 placed along their axes at a distance of $L = 15$ cm from each other. These tubes have a diameter of $d = 10$ mm and wall thickness of 0.5 mm, extending along the direction of heat transfer fluid flow.

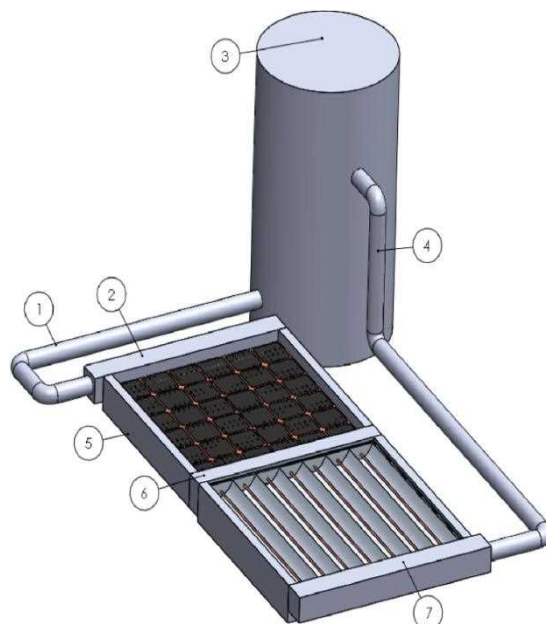


Fig. 1 Scheme of a CESHP with HTFPC (Combined Energy Supply System with Hybrid Thermal Photovoltaic Solar Collector) with a copper heat exchanger into a thermal accumulator.

Conventional symbols: 1, 4 - pipelines at the inlet and outlet of the HTFPC; 2, 7 – manifolds of the heat transfer fluid at the inlet to the photovoltaic panel and at the outlet of the thermal solar collector; 3 - thermal accumulator; 5 - photovoltaic panel; 6 – heat exchanger.

To measure the average temperature of the heat transfer fluid in the thermal storage tank 8, the entire filled volume of the tank was conditionally divided into three layers of equal height, where temperature is measured in the central plane of each layer by an thermocouple made of 4 mm thick glass, which measures the average temperature at four points on the body.

The cooled heat transfer fluid flows through copper pipeline 14 with a diameter $D = 25$ mm and a wall thickness of 0.5 mm through distribution manifold 16 into the photovoltaic panel, where it is heated by photocells 19 and enters the thermal solar collector.

The movement of the heat transfer fluid in the system, which is water, occurs using a circulation pump 13, which provides a flow rate of 0.03 kg/s in the circuit.

For electricity production, 36 silicon photocells measuring 155×155 mm and 0.3 mm thick are attached to the copper plate of the photovoltaic panel. To increase the efficiency of photocells by removing heat from them, the copper plate of the photovoltaic panel is connected to copper tubes of the CESHP circuit.

The research was conducted in SolidWorks 2022 using the FlowSimulation module under steady-state conditions: at ambient temperature to.c. = 15°C and solar radiation intensity $IT = 900 \text{ W/m}^2$, taking into account the HTFPC inclination angle to the horizon = 90° and the azimuthal angle of solar rays incidence on the HTFPC plane = 90° .

According to experimental studies, the temperature changes of the heat transfer fluid in HTFPC are shown in Fig. 2.

From Fig. 2, it can be seen that at a constant ambient temperature ta.t. equal to 15°C , the temperature of the heat transfer fluid in the pipeline at the HTFPC outlet t_{out} rapidly increased to 33°C during the first 20 minutes of the experiment, and then increased steadily to reach a final value of 43°C . The temperature of the heat transfer fluid at the HTFPC inlet t_{in} increased less intensively than t_{out} during the first 20 minutes, rising to 25°C , and then due to steady growth reached 35°C at the end of the experiment.

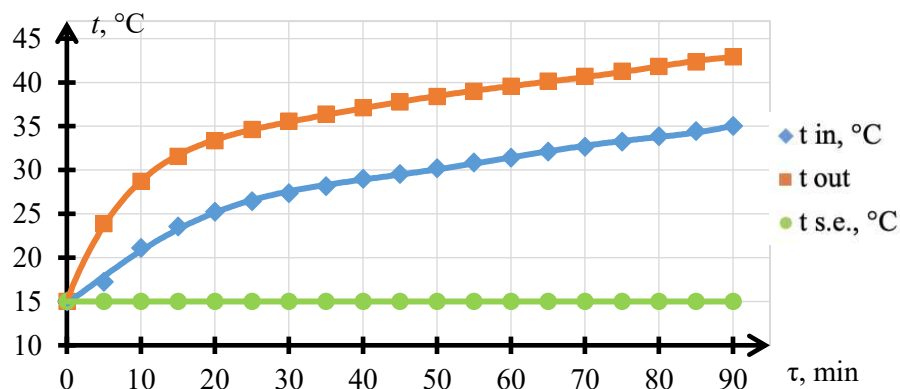


Fig. 2. Temperatures of the coolant in the pipeline at the inlet, t_{in} , °C, at the tout, outlet, °C, from HTFPC and the surrounding enviroment, $t_{s.e}$ °C.

Further research was conducted on the temperature changes of the heat transfer fluid in the thermal storage tank, which are shown in Fig. 3

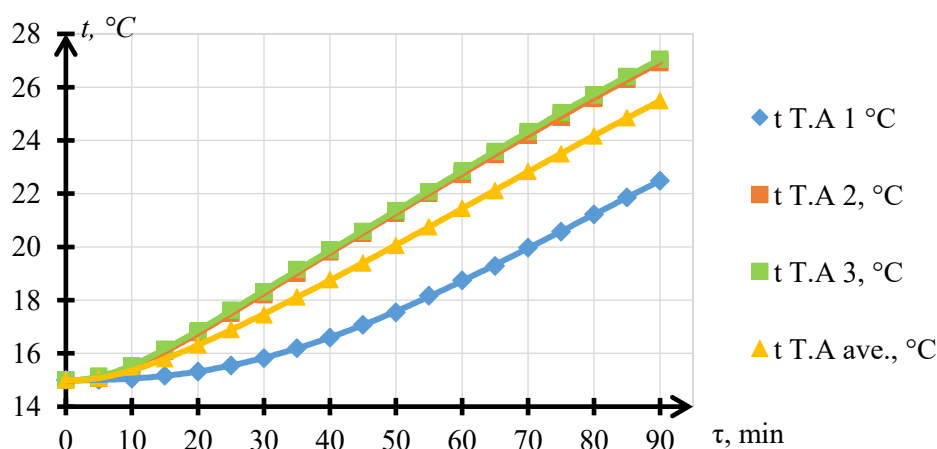


Fig. 3 Coolant temperatures in the thermal accumulator t_{TA} , °C, depending on the time of the experiment τ , min.

A According to Fig. 3, the average temperatures in the middle layer $t_{T.A2}$ and in the upper layer $t_{T.A3}$ of the heat transfer fluid volume in the thermal storage tank are almost identical throughout the experiment, begin to increase 5 minutes after the start of measurements, and reach 27°C at the end of the study. The temperature in the lower layer of the heat transfer fluid volume in the thermal storage tank $t_{T.A1}$ increases 10 minutes after the start of the research and reaches 22.5°C at the end of the experiment. The values of the average temperature of the heat transfer fluid volume in the thermal storage tank t_{TAavg} tend toward the values of $t_{T.A2}$ and $t_{T.A3}$, because in the upper part of the thermal storage tank, temperatures are higher and almost uniform compared to its lower part, and reach a maximum value of 25.5°C at the end of the experiment.

In Fig. 4, with no change in ambient temperature Δt_{in} , the temperature increase of the heat transfer fluid in the pipeline at the HTFPC outlet Δt_{out} rapidly rises to 18°C during the first 20 minutes of the experiment, and then, increasing steadily, reaches 28°C at the end of the study. The temperature increase of the heat transfer fluid at the HTFPC inlet Δt_{in} after 20 minutes from the start of measurements is less than Δt_{out} , rapidly increases to 10°C, and over the remaining time reaches 20°C through steady growth. In the thermal storage tank, the average temperature increase of the heat transfer fluid occurs uniformly from 5 min to 90 min, so $\Delta T_{A avg}$ increases by 10.5°C at the end of the experiment.

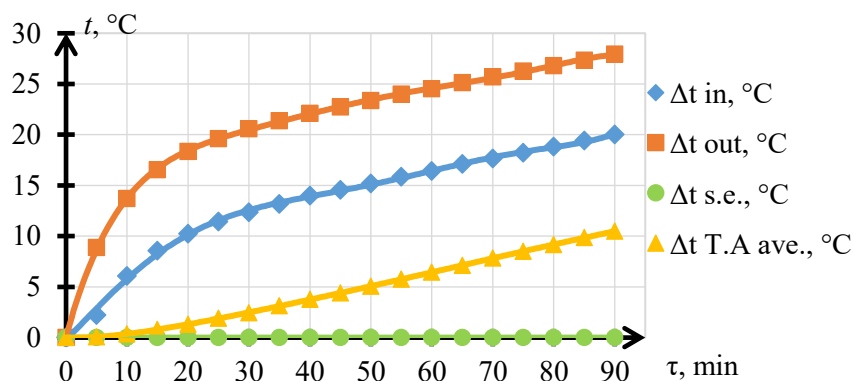


Fig. 4. Heat carrier temperature increase in the pipeline at the inlet Δt_{in} , °C, at the outlet Δt_{out} , °C, from the HTFPC, to the thermal accumulator $\Delta t_{T.A. apr.}$, °C, and the surrounding environment $\Delta t_{s.e.}$, °C.

Based on the analysis of CESHP with HTFPC operation modeling results, the following parameters were calculated: instantaneous specific power values of HTFPC; change in thermal efficiency of HTFPC during the experiment; instantaneous specific power of CESHP with HTFPC; thermal efficiency of CESHP with HTFPC during the experiment.

The instantaneous specific power values of HTFPC are shown in Fig.5. From this figure, it can be seen that after 15 minutes from the start of the experiment, the instantaneous specific thermal power of HTFPC Q_{HTFPC} stabilizes at 500 W/m².

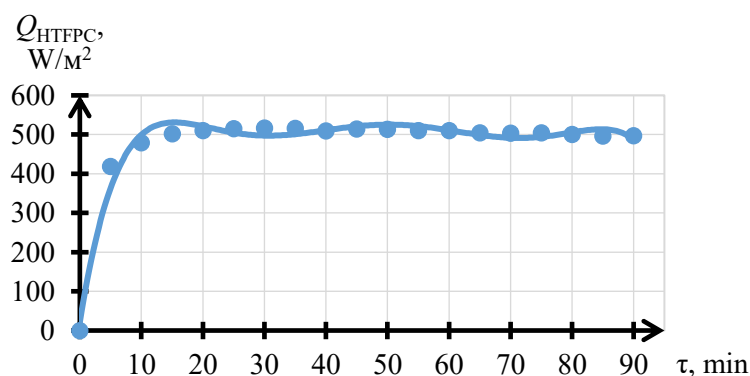


Fig. 5 Instantaneous specific heat capacity of HTFPC.

Discussion of Research Results

Most energy supply system modeling studies, such as [1,2], are conducted using mathematical methods. The authors, in turn, use computer modeling with specialized software, as in studies [3]. However, unlike [4], the authors also used computer software for analyzing and structuring the obtained results. Based on the computer modeling results, the change in instantaneous specific thermal power of the system with a hybrid thermal photovoltaic solar collector was determined, which, after 30 minutes, reaches a nominal value of 140 J/m². As shown in work [5], the time to reach stable collector operation is 30-40 minutes, depending on solar radiation power.

Referring to [6-8], we can determine the pattern of changes in thermal efficiency of the heat supply system with a hybrid solar collector from many different factors, such as tube placement, collector tilt angle, solar radiation power, and construction materials.

Regarding thermal process modeling, [9] describes a new hybrid collector combined with a switchable heat pump system to improve electricity generation by photovoltaic panels and efficient use of solar thermal energy, which can meet heating needs in winter and cooling in summer.

Initially, an energy model and exergy model of the system were developed, and numerical modeling was conducted in MATLAB based on the energy and exergy models. Then, the thermodynamic characteristics of the system with different working fluids were investigated and compared. These are very valuable studies to process, as the authors of this article used only water as a heat transfer fluid, and after comparison with other scientists' research, it can be stated that in both models, energy efficiency will increase by 5-10% due to heat removal from under silicon elements, indicating the relevance of this research field.

Conclusions

A thermal efficiency modeling system with a hybrid thermal photovoltaic solar collector has been developed, which made it possible to determine the main thermophysical characteristics of the energy system with a storage tank based on selected factors. Since the global scientific community recommends intensifying the use of renewable energy sources, and according to European energy and climate strategies, energy production from solar sources is planned to increase significantly.

A model of a system with a new hybrid solar collector has been developed that can simultaneously produce thermal and electrical energy. Using this model, the change in heat transfer fluid temperatures in the hybrid thermal photovoltaic solar collector was studied as a function of irradiation time, as well as in the thermal storage tank.

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Optimizing Coal Fine Properties for Industrial Applications Through Chemical Treatments

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Abstract. *This study examines how different solvents affect the textural properties of coal fines through controlled washing. The findings reveal that solvent type and washing duration significantly impact surface area and pore volume. These insights are valuable for optimizing coal fines in adsorption, filtration, and catalytic applications, enhancing their industrial potential.*

Coal fines, surface area, pore volume, solvent washing, adsorption.

Introduction

Coal fines, fine particulate byproducts of coal processing, have significant adsorption potential due to their porous structure. However, their effectiveness in industrial applications depends on surface area and pore volume [1-3]. Modifying these properties can enhance their utility in filtration, catalysis, and gas storage.

One widely used method to improve porous materials is chemical or solvent washing, which removes surface contaminants and alters the microstructure [4]. Solvent selection plays a crucial role in determining the final textural properties of coal fines.

A particularly promising application of these modified materials is in activated carbon production. Activated carbon, characterized by high porosity and adsorption capacity, is extensively used in water purification, air filtration, and energy storage [5]. By refining coal fines through solvent treatment, their properties can be tailored for specific adsorption-based applications, including carbon dioxide capture and catalytic reactions.

This study investigates the effects of different solvent treatments on the surface area and pore volume of coal fines, providing insight into optimizing their textural properties for various industrial applications.

Materials and Methods

A sample of coal fines (particle size: 0–3 mm) was obtained from commercially available products supplied by LLC Perechin Timber and Chemical Plant. The sample underwent washing using various solvents to assess changes in its textural properties. To ensure complete washing, a fixed solvent-to-coal ratio of 3:1 (volume/mass) was maintained. The washing process involved controlled heating and refluxing to prevent solvent loss, with specific durations set for each solvent. All solvents used in the study were procured from Sigma-Aldrich to ensure consistency and reliability of the results.

Following the washing process, the key textural parameters – specific surface area (m^2/g) and pore volume (cm^3/g) – were determined to evaluate the impact of each solvent treatment. The processed carbon materials were then subjected to further preparation and analysis. They were sieved using a 0.16 mm mesh to remove oversized particles and subsequently degassed with nitrogen at 300°C for one hour using a Micromeritics FlowPrep 060 degassing system. The final

measurements of surface area and pore volume were performed using a Micromeritics Gemini VII porosimeter, following the instrument's standard operating procedures.

Results and Discussion

This study investigates the influence of various solvents on the textural properties of coal fines through a controlled washing process. The primary objective was to evaluate the modifications in specific surface area and pore volume after washing with different solvents. The results indicate that solvent type and washing duration significantly affect these properties, providing valuable insights for potential applications in adsorption and filtration technologies. Coal fines, fine particulate matter derived from coal processing, possess significant surface and pore characteristics that influence their applications. Enhancing these properties through washing with different solvents can lead to improved performance in adsorption and catalytic processes. This study aims to determine how different solvents affect the surface area and pore volume of coal fines, using a comparative experimental approach. A sample of coal fines (particle size: 0–3 mm) was subjected to washing using various solvents. A fixed solvent-to-coal ratio was maintained at 3:1 (volume/mass) to ensure complete washing. The washing process involved heating and refluxing for controlled durations, preventing solvent loss. The specific washing conditions for each solvent were as follows: ethyl acetate, ethanol, and acetic acid were boiled for 1 hour under reflux; water was boiled for 2 and 5 hours under reflux; 5% aqueous orthophosphoric acid solution was boiled for 2 hours under reflux; and 10% aqueous potassium hydroxide solution was washed at room temperature for 24 hours. After washing, the specific surface area (m^2/g) and pore volume (cm^3/g) of the samples were determined as key indicators of textural changes. The results of the washing process are summarized in the following Table 1:

Table 1

Changes in surface area and pore volume of coal fines after washing with various solvents

Solvent	Boiling Time (h)	Surface Area (m^2/g)	Pore Volume (cm^3/g)
Acetic acid	1	196.0	0.1188
Control (unwashed)	-	215.5	0.1428
Ethyl acetate	1	227.7	0.1802
Water	2	237.2	0.1769
Ethanol	1	254.0	0.1989
5% Orthophosphoric acid	2	258.0	0.2050
Water	5	263.2	0.1709
10% Potassium hydroxide	24 (room temp)	372.1	0.1710

The best sample after the experiment was the coal fines washed with 10% potassium hydroxide, which exhibited the highest surface area ($372.1 \text{ m}^2/\text{g}$). This sample can be particularly valuable in applications such as gas adsorption, activated carbon production, and catalytic processes due to its enhanced surface properties. These characteristics make it suitable for use in environmental cleanup technologies, industrial filtration, and energy storage materials. The increase in surface area and porosity directly correlates to improved adsorption capabilities, which are crucial for processes like pollutant removal, chemical separation, and catalyst support in industrial applications.

The control sample of unwashed coal fines exhibited a surface area of $215.5 \text{ m}^2/\text{g}$ and a pore volume of $0.1428 \text{ cm}^3/\text{g}$, serving as a baseline for comparison. Washing with ethanol,

orthophosphoric acid, and potassium hydroxide resulted in a significant increase in both parameters. Ethanol and orthophosphoric acid yielded the highest pore volumes ($0.1989 \text{ cm}^3/\text{g}$ and $0.2050 \text{ cm}^3/\text{g}$, respectively), suggesting effective removal of surface impurities and opening of microstructures. The treatment with potassium hydroxide resulted in the most considerable increase in surface area ($372.1 \text{ m}^2/\text{g}$), likely due to its strong chemical reactivity, which can break down complex organic structures and dissolve inorganic components. Prolonged washing with water (5 hours) also significantly increased surface area, indicating that extended exposure to a polar solvent aids in the gradual removal of loosely bound materials. In contrast, acetic acid washing led to a decrease in both surface area and pore volume, likely due to the deposition of reaction products on the coal surface or partial collapse of micropores. These data are visualized in Fig. 1.

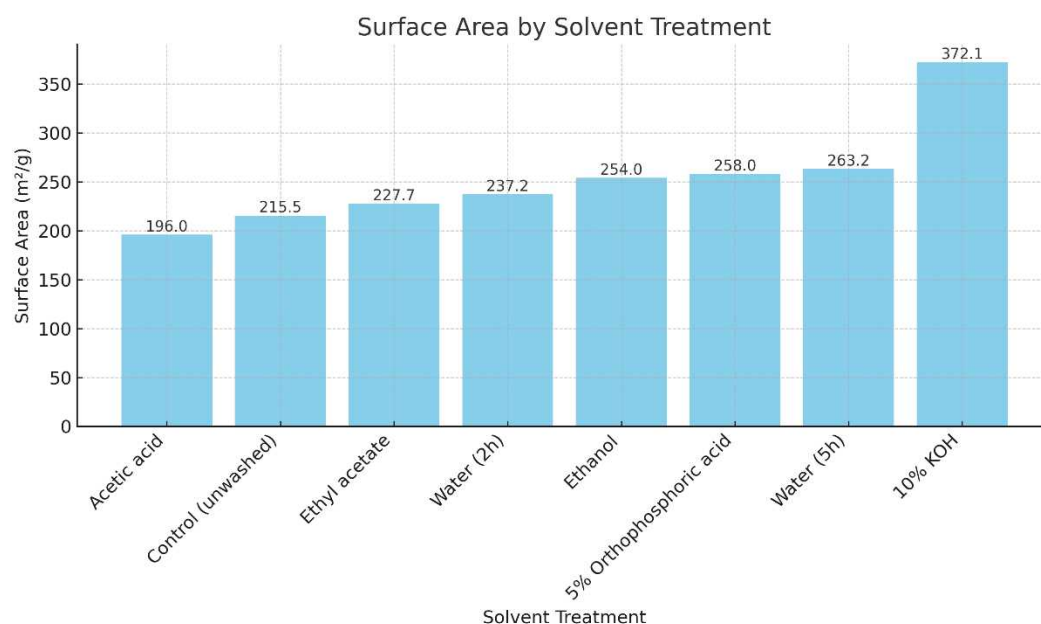


Fig.1. Comparison of surface area (m^2/g) for different solvent treatments.

These observations can be explained through chemical interactions. Potassium hydroxide, being a strong base, can facilitate the hydrolysis of organic compounds and the dissolution of certain mineral components, leading to an increase in surface area. Ethanol, as an organic solvent, may remove non-polar hydrocarbons more effectively, exposing a higher number of adsorption sites. Orthophosphoric acid, a weak acid, could react with basic functional groups present in coal, modifying the structure and increasing porosity. Water, particularly with prolonged exposure, can induce physical swelling and dissolution of certain soluble compounds, contributing to the observed increase in textural properties. The observed differences emphasize the importance of solvent selection in modifying coal fines for industrial applications such as adsorption, catalysis, and filtration. Further studies should focus on the specific chemical transformations occurring during washing to better understand the mechanisms underlying these textural modifications.

Potassium hydroxide treatment: properties, uses, and benefits

The potassium hydroxide-treated sample exhibits a highly developed porous structure with distinct micro- and mesoporous contributions. A single-point measurement ($p/p^\circ \approx 0.25103$) indicates a surface area of $154.07 \text{ m}^2/\text{g}$, while BET analysis reveals a significantly larger value of $322.08 \text{ m}^2/\text{g}$, highlighting the extensive surface area accessible through multilayer adsorption. The t-Plot method further refines this assessment, attributing $175.80 \text{ m}^2/\text{g}$ to micropores and $146.29 \text{ m}^2/\text{g}$ to external (meso- and macroporous) surfaces, confirming the coexistence of both pore types.

BJH analysis, which evaluates pores within the 5,000–5,000,000 Å range, estimates a cumulative surface area of 270.30 m²/g, underscoring the mesoporous fraction's contribution. Pore volume measurements reinforce this trend—single-point adsorption at low relative pressure ($p/p^\circ = 0.01$) yields a total pore volume of 0.01120 cm³/g for pores below 9,384 Å, closely matching the t-Plot micropore volume (0.01134 cm³/g). However, BJH analysis registers a significantly higher cumulative pore volume (0.17137 cm³/g), indicating a substantial mesopore presence. The average pore width, determined via BJH, is 25.36 Å, positioning the sample squarely in the mesoporous regime.

Further refinement using DFT analysis detects no measurable volume in pores smaller than 13.08 Å, with a total pore volume of 0.16048 cm³/g up to 448.83 Å and a corresponding pore area of 144.32 m²/g for pores above 13.08 Å. This confirms that the majority of the accessible surface area originates from larger pores. The Horvath-Kawazoe method, particularly sensitive to micropores, indicates a dominant micropore width around 12.55 Å, with a maximum pore volume of 0.05082 cm³/g at a relative pressure of 0.15104.

The adsorption isotherm provides insight into the sample's gas uptake behavior, showing a steady increase in adsorption volume as relative pressure rises (Figure 2). While the overall trend follows a smooth uptake, a few later data points display anomalous negative values, likely due to instrumental artifacts rather than actual material behavior.

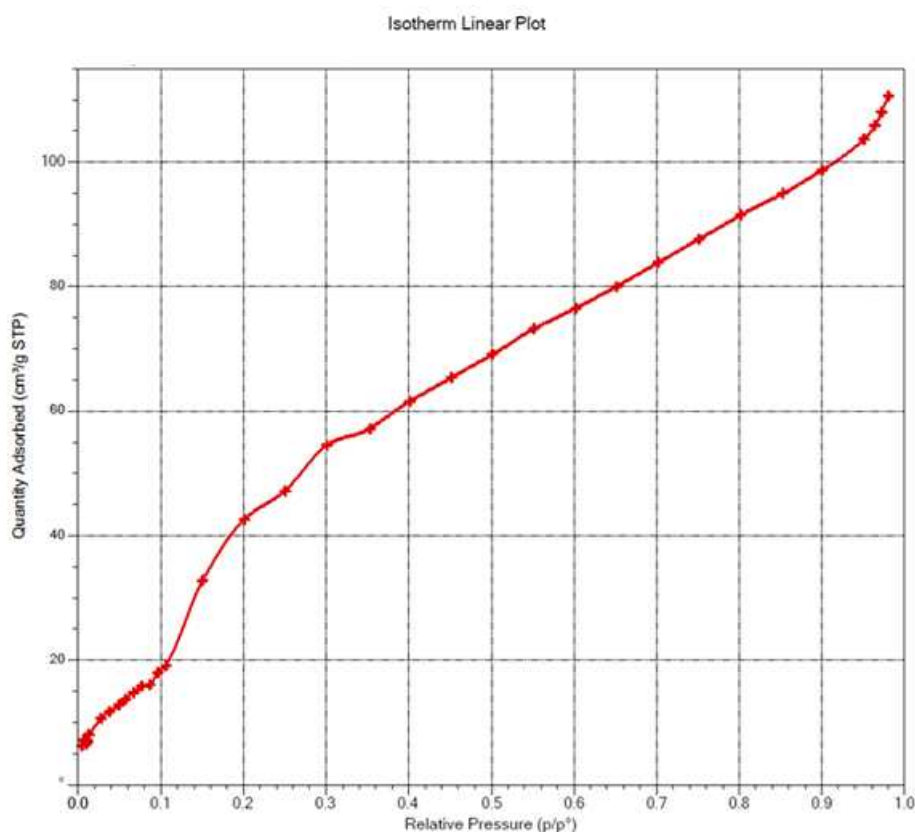


Fig.2. Adsorption isotherm of the KOH-treated sample.

These results confirm that KOH treatment significantly enhances porosity, yielding a material with a well-balanced network of micropores and mesopores. This improved textural profile makes KOH-treated coal fines highly suitable for adsorption, catalysis, and energy-related applications. The increased surface area enhances gas adsorption efficiency, particularly for carbon dioxide and methane capture, making the material valuable for carbon sequestration and energy storage. Its enhanced porosity also makes it an excellent precursor for activated carbon, widely used in water purification, air filtration, and chemical separation processes. Additionally,

the material's high surface area makes it an effective support for catalysts in industrial reactions such as hydrocarbon cracking and hydrogen production. Its improved electrical conductivity further suggests applications in energy storage devices, including supercapacitors and lithium-ion batteries.

Future research should focus on the long-term stability, cost-effectiveness, and large-scale feasibility of this treatment method to optimize its industrial application.

Conclusions

This study demonstrated that washing coal fines with different solvents significantly alters their textural properties, with potassium hydroxide treatment leading to the most substantial increase in surface area. The observed modifications suggest potential applications in adsorption, filtration, and catalytic industries. Understanding the chemical interactions between coal fines and various solvents provides valuable insights into optimizing the efficiency of coal-based materials for environmental and industrial use. Future research should explore the detailed mechanisms of these modifications and their long-term stability in practical applications.

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Preparation and Structure of Chitosan-Based Porous Scaffolds for Potential Application in the Treatment for Diabetic Foot Complications

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Abstract. *As a result of this study, porous chitosan (CS) - based scaffolds loaded with cellulose nanocrystals (CNCs) and graphene (GF) were successfully fabricated using a freeze-drying method. In particular, the effect of fillers on the structure of the obtained materials was investigated.*

Keywords: chitosan, cellulose nanocrystal, graphene, wound-dressing, antimicrobial properties.

Introduction

The healthy wound healing process is a dynamic and well-organized physiological process, involving different biological events, controlled by different cell types [1, 2]. Besides, several common comorbidities (including diabetes, vascular, and autoimmune diseases) can often interfere with the normal healing phase [3].

The elderly, patients with diabetes, and patients with genetic disorders are especially predisposed to abnormal wound healing, which leads to the formation of chronic wounds. Therefore, there is a need to continuously increase the effectiveness of wound treatment methods [4]. Potentially, some microorganisms from the skin surface can penetrate the adjacent appendages and glands, which in some cases can play a harmful role and cause infection [5-7].

Chitosan has been the focus of great attention due to its properties, such as nontoxicity, biocompatibility, biodegradability, adsorption properties, and low price [8, 9]. CS exhibits excellent biocompatibility and immune modulator properties, which are crucial for promoting wound healing [10, 11]. It has been widely investigated as an antimicrobial agent for preventing and treating infections owing to its intrinsic antimicrobial properties, and also its ability to effectively deliver extrinsic antimicrobial compounds into the infected area [12]. To reinforce and stabilise pure CS-scaffolds, cross-linkers are commonly used [13]. Because chitosan is polycationic, it can interact with polyanions to form polyelectrolyte complexes. These characteristics allow it to be used in various materials, including sponge scaffolds.

Genipin (GP) is a safe and non-toxic natural cross-linking agent of plant origin. GPs are commonly used in medicine [14, 15]. Compared with traditional agents, CS modifies the amino genipin, and its mechanical properties were significantly enhanced, and the hydrogel crosslinked with genipin is less cytotoxic [16]. Owing to its high biocompatibility, GP has recently been used as a novel cross-linking reagent to replace traditional cross-linking agents. It can react spontaneously with amino groups or proteins or chitosan to form dark-blue pigments. GP has also been found to be 10,000 times less toxic than glutaraldehyde [17].

Cellulose nanocrystals, in the form of rod-like or whisker-shaped highly crystalline nanostructures whose length is significantly (10-40 times) larger than the cross-section [18], may result from the acid hydrolysis of agricultural cellulose-containing products [19]. CNCs are bio-based and renewable nanosized materials that can be derived from plants or bacteria, and in general, from a variety of highly available and renewable cellulose-rich sources of the most abundant natural polymers [20].

Graphene and its derivatives have lately been employed as a filler within a polymer matrix to confer antimicrobial properties [21]. In fact, GF has proved a broad range of antimicrobial activity toward bacteria, fungi, and viruses [22], by damaging the bacterial membrane, interrupting the cell cycle, or inducing bacterial cell death through inflammatory cascade activation [23].

The main driving idea of this work was the development of an easy-to-handle scaffold able to yield stage-specific treatment and accelerate wound healing, especially with chronic wounds in the diabetic foot. To this aim, CS-based scaffolds containing CNCs and GF nanoplatelets and ionically crosslinked with GP we successfully prepared by an easy and scalable freeze-drying process. Different concentrations of CNCs and GF nanosheets were adopted. The effect of single and simultaneous loading of CNCs and GF nanosheets within CS spongy-like scaffolds was investigated in terms of morphological, structural, physico-chemical, pro-regenerative, and antimicrobial properties.

1. Results and Discussion

1.1. Preparation of CS-based scaffolds functionalised with CNC/GF, crosslinked with GP

CS-based hybrid scaffolds with CNCs, GF, and GP were prepared by the freeze-drying method, as represented in Fig. 1, according to the modified methodology in the article [24]. CS powder (1.67% w/v) was dissolved in 1%w/v lactic acid aqueous solution under stirring at 60°C for 3 hours. Suspension of CNC in water in an amount of 10 and 50%w_{CNC}/w_{CS} calculated to CS weight, and GF solution (1% w_{GF}/w_{CS}) were added to the CS slurry and stirred at room temperature until reaching a homogeneous dispersion. Next, a solution of genipin (GP) in an amount of 1% w_{CS} was added, and the reaction mixture was stirred for another hour. The slurries were poured into bottles with a diameter of 6 cm, using a volume of suspension corresponding to 6 mm of height, and underwent a freeze-drying process (equilibration at 4 °C for 30 min, freezing at –60 °C for 24 h, and drying at –80 °C for 48 h under vacuum in a freeze dryer. Afterward, cylindrical scaffolds (d = 6 mm, h = 6 mm) were obtained.

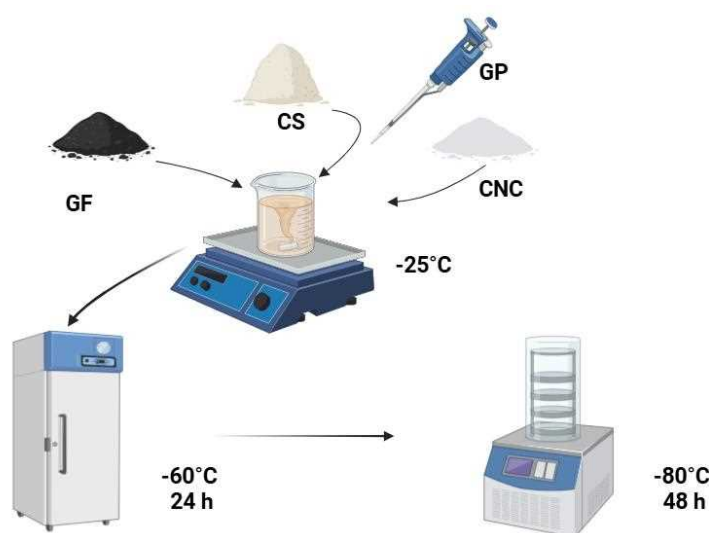


Fig.1. Schematic of the process of making scaffolds: preparation of solutions and crosslinking reaction (1); freezing of samples (2), and freeze drying processes (3). Created with BioRender.com.

1.2 Characteristics of the morphology of the obtained materials

CS/CNC/GF scaffolds morphology was investigated through JSM 7200F field emission scanning electron microscope (Jeol, USA) at an accelerating voltage of 10 kV and 15 kV.

These SEM micrographs of scaffolds' cross sections show the single loading effect of CNC. The addition of cellulose nanocrystals leads to a decrease in pore diameter, which is especially

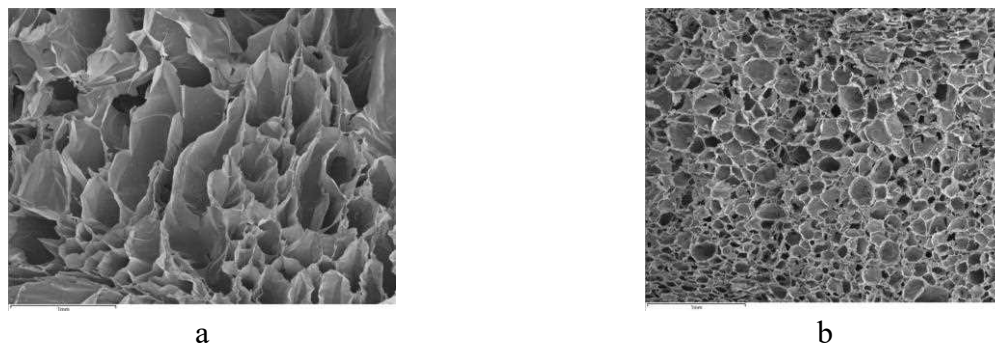


Fig. 2. The morphology of CS scaffold (a) and scaffold with 50% nanocrystals (b) [Mag. 200 $\times$, scale bar 1 mm].

noticeable for composites with a cellulose nanocrystal concentration of 50% (Fig.2, b). Adding graphene to the chitosan solution can also have an impact on reducing pores. This effect resulted from non-covalent interactions between the highly electronegative GF and the polycationic CS matrix [23]. In terms of pore size, the influence of GF loaded within the neat CS scaffold was evaluated.

Conclusions

In this study, we developed scaffolds that encompassed multifunctional features to improve wound healing. The scaffolds were composed of CS, CNC, GF with GP crosslinking. In this work, the effect of single and simultaneous loading of CNC and GO as reinforcement and antimicrobial filler, respectively, into the CS matrix was systematically analyzed. It was found that CNC loading alone stabilized the CS-based scaffolds when used at a lower concentration. GF loading could positively affect the mechanical and antimicrobial properties of the resulting materials.

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Plant Oil-Based Polymers: Synthesis, Structure, and Temperature-Responsive Properties Near Physiological Temperatures

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Abstract. *Acrylic monomers derived from palm (PMM), hydrogenated sunflower (HFM), and castor (CSM) oils were polymerized to explore phase transitions. DSC analysis revealed semicrystalline structures in poly(HFM) and poly(PMM) and an amorphous structure in poly(CSM). The synthesized polymers exhibit a wide range of glass, melting, and flow transition temperatures, with some close to the physiological range, highlighting potential biomedical applications and polymer brushes development.*

Keywords: Thermal behavior, biobased polymers, phase transition temperatures, temperature-responsive polymers.

Introduction

The development of sustainable polymers derived from renewable resources has garnered significant attention as an environmentally friendly solution to mitigate synthetic polymer waste pollution [1]. Among renewable resources, plant oils are particularly promising due to their abundance, low cost, and adaptability to a variety of chemical modifications [2,3]. These oils, composed of triglycerides with C₁₂–C₂₂ fatty acid chains, as a rule, possess double bonds or functional groups such as hydroxy and epoxy, which enable their transformation into monomers and polymers [4,5]. A major challenge in this field lies in the conversion of triglycerides into monomers with precisely tailored properties. This is predominantly achieved through reactions involving ester groups, such as hydrolysis [6], amidation [7], and transesterification [8], alongside double-bond modifications like hydrogenation [9]. Polymers synthesized from amide-functionalized monomers exhibit a wide range of glass transition temperatures (T_g), enabling their application in diverse domains ranging from elastomers to rigid plastics [10].

Recent advancements have introduced efficient methods for synthesizing plant oil-based acrylic monomers (POBMs). For instance, D. Delatte et al.[10] developed soybean oil macromonomers through amidation and acrylation reactions. Similarly, one-step transesterification with N-(2-hydroxyethyl)acrylamide has been employed to produce monomers from various plant oils, including olive and soybean oils [11,12]. The resulting polymers exhibit varying T_g values depending on the fatty acid composition. Olive oil-based polymers, for example, display T_g values near room temperature, while soybean oil-based polymers, characterized by higher levels of unsaturation, exhibit T_g values below 0 °C [13,14]. These tunable thermal properties are particularly relevant for biomedical applications that require materials capable of

undergoing phase transitions near physiological temperatures. For example, poly(*N*-isopropyl acrylamide) (PNIPAM) exhibits a lower critical solution temperature (LCST) of 30–33 °C, enabling temperature-responsive behavior for tissue engineering. PNIPAM-based copolymer brushes can change their antibacterial and antifouling properties depending on ambient temperature [15–18]. Additionally, poly(*n*-butyl methacrylate) (PBMA) brushes demonstrate T_g values ranging from 13 to 25 °C, influencing protein adsorption and cell adhesion [19,20]. Plant oil-based polymers thus represent a sustainable and versatile alternative to synthetic counterparts, offering tunable thermal and mechanical properties. Saturated fatty acids promote the formation of crystalline domains, enhancing rigidity, while unsaturated fatty acids confer flexibility, making these materials highly promising for advanced biomedical applications.

Results

We proposed the synthesis of POBMs derived from palm, hydrogenated sunflower and castor oils, and their homo- and copolymers, using advanced methods [11]. The POBMs were synthesized through a one-step transesterification reaction between each oil and *N*-(2-hydroxyethyl)acrylamide, with KOH serving as the catalyst. Their structures were confirmed by ^1H NMR spectroscopy, as illustrated in Fig. 1, with key signals indicating the presence of *N*-acryloyl amide fragments, fatty acid residues, and additionally the presence of hydroxyl groups in the monomer derived from castor oil. The phase transition temperatures of the synthesized POBMs were analyzed using differential scanning calorimetry (DSC). For castor oil and its derived monomer (CSM), DSC measurements exhibited glass transition temperatures rather than crystalline melting, suggesting the formation of mostly amorphous structures.

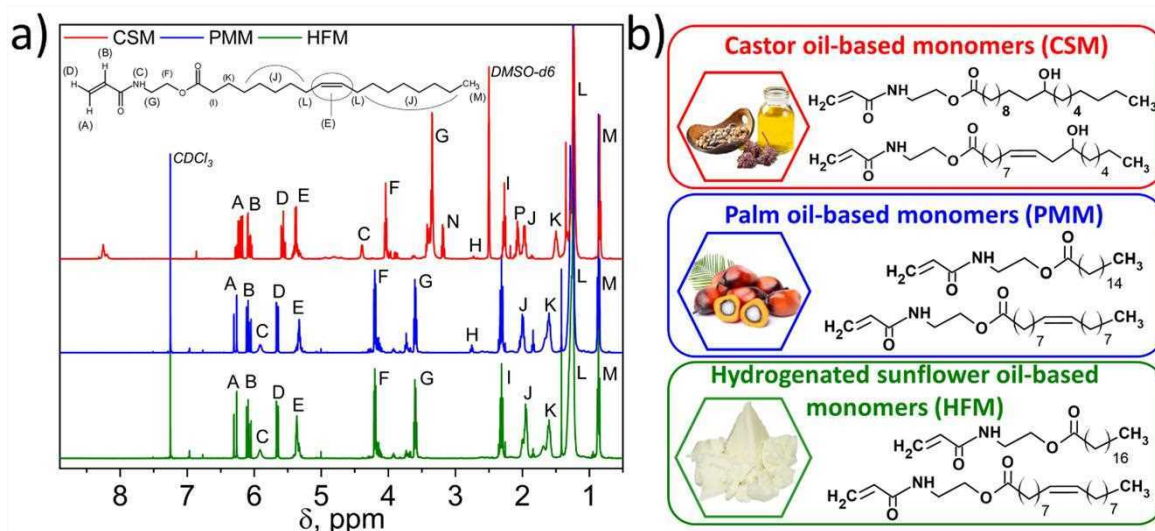


Fig. 1. ^1H NMR spectra (a) and chemical structures (b) of monomers from castor, palm, and hydrogenated sunflower oils.

This behavior is likely due to the high ricinoleic acid content with hydroxyl groups, which restricts conformational mobility at low temperatures. In contrast, the DSC curves for PMM and HFM showed two distinct endothermic peaks, corresponding to melting transitions at 10 °C and 53 °C for PMM, and 37 °C and 49 °C for HFM. These findings indicate the presence of two distinct monomeric components in both HFM and PMM, consistent with the results obtained from mass spectrometry analysis.

DSC thermograms presented in Fig. 2a show that homopolymers derived from PMM and HFM are semicrystalline, while the homopolymer from CSM is amorphous. These thermal transitions are attributed to the formation of ordered domains, caused by the presence of saturated palmitic and stearic acid fractions in the homopolymers from PMM and HFM. For copolymers

containing styrene (Fig. 2b), two distinct transitions are evident: one associated with the mobility of the long alkyl fatty acid side chains and the other with the macromolecular backbone. For the copolymers derived from PMM and HFM, comparable transition temperatures are observed, whereas the second transition occurs at 35 °C for the castor oil-based copolymer. This higher value is likely due to the hydroxyl groups in the ricinoleic acid residues, which serve as additional chain transfer sites, promoting the formation of more rigid macromolecules corresponding to the fractions enriched with polystyrene fragments.

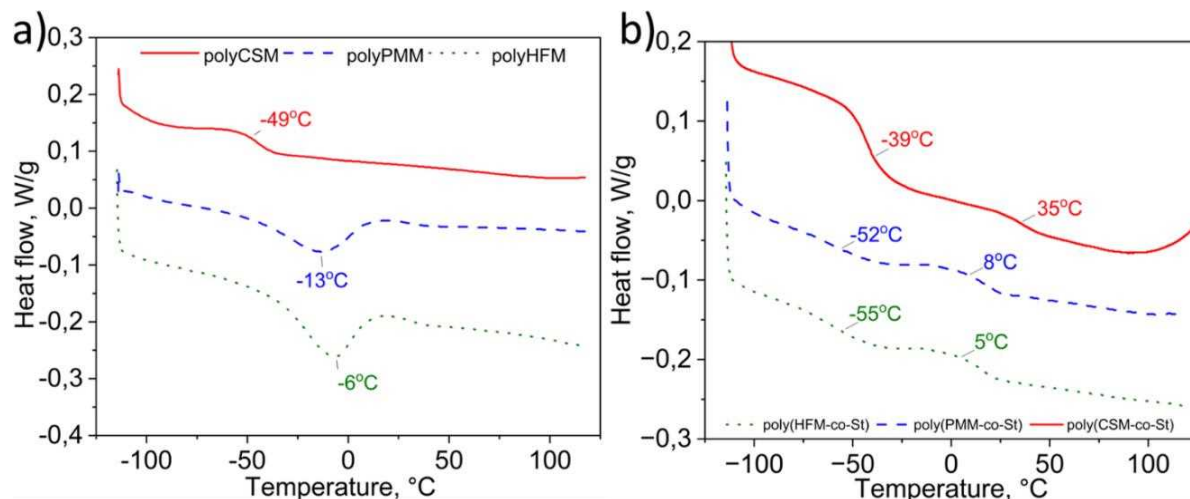


Fig. 2. DCS thermograms of POBMs homo- and copolymers with styrene.

Conclusion

In this work, we demonstrate that the synthesized homo- and copolymers based on POBMs exhibit a broad range of phase transition temperatures, with some polymers having transition temperatures near to physiological range. This behavior is attributed to the unique structures of the polymers and the presence of an intramolecular plasticization effect. These properties are crucial for the development of "smart" polymer systems, such as polymer brushes, that undergo temperature-induced transitions near to the physiological range.

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Mass Transfer During the Dissolution of Ammonium Tetrafluoroborate, Based on the Theory of Locally Isotropic Turbulence

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Abstract. *Mass transfer of dissolution of ATFB, depending on the temperature of the solution and the stirring frequency, was investigated. Mass transfer coefficients have been experimentally determined and compared with theoretically determined ones. A computational dependence has been obtained, depending on the temperature of the solution and the stirring frequency.*

Keywords: mass transfer coefficient, Ammonium Tetrafluoroborate, dissolution, blade agitator, mechanical mixing, diffusion, frequency, temperature of the solution, locally isotropic turbulence.

Introduction

Ammonium Tetrafluoroborate (ATFB) is a crucial compound with diverse applications across multiple industries, including electronics, glass manufacturing, and metal finishing. In the electronics sector, it plays a key role in semiconductor and circuit board production, enhancing the adhesion of protective coatings. The glass industry utilizes ATFB to improve the strength and quality of glass products, while in metal finishing, it contributes to refining surface properties, ensuring a polished and durable finish. As the demand for high-performance materials continues to grow, the adaptability and effectiveness of Ammonium Tetrafluoroborate make it an indispensable component in modern manufacturing.

A great advantage of mineral compounds is their traditional and very convenient form of supply in the form of granules. Substances in granular form have better physicochemical properties compared to powdered form. Granulation significantly reduces the susceptibility of the product to caking, and thus simplifies storage, transporting, and dosing [1].

Literature review

Suspension of solids in mechanically agitated vessels plays a crucial role in various industrial solid-liquid processes, such as dissolution and leaching. This is particularly significant for process intensification, where high solids concentration slurries are processed to enhance throughput per unit volume without significant modifications to the existing infrastructure. Achieving off-bottom suspension in such systems requires a substantial increase in impeller speed and power draw. However, this does not necessarily guarantee improved solid-liquid mass transfer. While solid-liquid mass transfer in agitated vessels has been extensively studied over the past few decades. Limited research has explored the influence of active particle mass fraction on solid-liquid mass transfer in agitated vessels.

Numerous methodologies, calculation dependencies, and theoretical models have been proposed to study mass transfer processes in solid-liquid systems. Notably, the theory of isotropic turbulence [2,3] and the slip velocity theory [4] have been applied to model the mass transfer from particles to stirred liquids. However, these theories and calculation dependencies are based on specific assumptions and simplifications. As a result, several researchers have focused on assessing the accuracy of these models in predicting dissolution processes in industrial-scale stirred reactors [5] and identifying the relationship between impeller diameter and reactor size [6].

Most of the studies mentioned have been conducted using a single sphere or a stationary layer of substance. The originality and novelty of our research lie in the fact that the spheres in our study move freely within the reactor, interact with each other, and make contact with the liquid. This approach more accurately reflects the dissolution process during mechanical stirring under industrial conditions.

In summary, the literature highlights the importance of studying mass transfer processes in solid-liquid systems, predicting methods to intensify these processes, and utilizing models.

Experimental part

This paper presents the results of experimental studies of mass transfer during the collective dissolution of granules of ammonium tetrafluoroborate (ATFB) by mechanical mixing, according to the theory of isotropic turbulence. The study was carried out at different temperatures and stirring frequencies.

The methodology of the experimental part of the study is shown in [7]. According to the same methodology, experiments were conducted at temperatures of 293, 303, 313, and 323 K and impeller rotation frequencies of 1.67, 3.33, 5, and 6.67 s⁻¹.

Theoretical part

The calculation of the mass transfer coefficient during the dissolution process is based on the kinetic equation of mass transfer:

$$\frac{dM}{d\tau} = \beta \cdot F \cdot (C_s - C_\tau), \quad (1)$$

where is M – mass of the ball at the time of measurement, kg;

C_τ, C_s – current concentration and saturation concentration of ATFB in solution, kg/m³;

β – mass transfer coefficient during dissolution, m/s;

F – surface area of the sphere, m²;

Integrating Eq. (1) within the time change from 0 to τ , we obtain the following dependence of the mass transfer coefficient on the dissolution time: τ

$$\beta = \frac{M_0 - M}{F \cdot (C_s - C_\tau) \cdot \tau} \quad (2)$$

where M_0 – initial mass of the ATFB sphere, kg;

τ – residence time of ATFB sphere in the heat-resistant beaker, s;

The average surface of the balls involved in mass transfer was determined by the dependence:

$$\bar{F}_{i,j} = \sum \frac{\pi \cdot (d_{i,j}^2 + d_{i,j-1}^2)}{2}, \quad (3)$$

where $i = 1, 2, 3, \dots, 10$ is the period of time spent by the spheres in the heat-resistant beaker

$j = 1, 2, 3, \dots, 5$ is the number of ATFB spheres participating in the experiment.

d_i – the diameter of the sphere, at a point in time, τ_i

d_{i-1} is the diameter of the sphere at the initial time of the experiment.

The concentration of ATFB in the solution over a period of time τ was determined from the dependence of:

$$C_\tau = \frac{M_0 - M}{W}, \quad (4)$$

The average value of ATFB $\overline{C_\tau}$ concentration in the solution was determined by the following equation:

$$\overline{C_\tau} = \sum \frac{C_{k+1} + C_k}{2}, \quad (5)$$

where C_k – the current concentration of ATFB in the solution ($C_0 = 0, \tau = 0$), kg/m³,

W – the volume of liquid in the beaker ($W = 2.5 \cdot 10^{-3}$, m³).

For comparing the experimentally determined coefficient β_e , with a theoretically calculated one, a theoretical method based on the theory of locally isotropic turbulence was chosen. The subject of turbulence modeling is an infinite number of connections between individual particles of a system, which results in the processes of mass transfer, momentum, energy, and heat. Usually, these interactions are characteristic of turbulent flow. Under the conditions of mechanical mixing, the mass transfer coefficient β_{RT} was determined from the dependence given in [8]:

$$\beta_{RT} = 0.267 \cdot \left(\varepsilon_0 \cdot \frac{\mu}{\rho} \right)^{\frac{1}{4}} \cdot Sc^{-\frac{3}{4}}, \quad (6)$$

where ε_0 is the specific dissipation rate, W/kg;

ρ – density of the liquid kg/m³;

μ – dynamic viscosity of the liquid, Pa·s;

Sc – Schmidt number;

The Schmidt number was determined by the formula:

$$Sc = \frac{\nu}{D}, \quad (7)$$

where is ν the coefficient of kinematic viscosity of the solvent, m²/s;

D – molecular diffusion coefficient of ATFB in solution, m²/s.

The diffusion coefficient was determined by the method of Wilke and Cheng [9], from the equation:

$$D_{12}^0 = 7.4 \cdot 10^{-8} \left[\frac{(\varphi \cdot M_2)^{1/2} \cdot T}{\mu \cdot V_1^{0.6}} \right], \quad (8)$$

where is D_{12}^0 the coefficient of mutual diffusion of the substance to be dissolved 1 in solvent 2 at a very low concentration of the substance to be dissolved, cm²/s;

M_2 – molecular weight of the solvent, a.u.m.;

T – temperature, K;

V_1 – mole volume of the solution at its normal boiling point, m³/mol (determined by the group components of Le Ba);

φ – the "association parameter" of the solvent (for water = 2.6, [9]);

The specific energy of dissipation ε_0 was determined by the power consumption for mixing and their attribution to the mass of the liquid in the volume of the device.

The mixing power of a mechanical stirrer was determined according to [8]:

$$N = K_N \cdot \rho \cdot n^3 \cdot d_M^5, \quad (9)$$

where K_N is the mixing coefficient, which was determined by the Reynolds number;

d_M – diameter of the stirring blades, m;

n – stirring frequency s⁻¹.

The specific value of the dissipation energy per unit mass of the liquid according to [16]:

$$\varepsilon_0 = \frac{N}{\rho \cdot V}, \quad (10)$$

where V is the volume of the liquid, m^3 ;

N – mixing power, W.

The values of the mass transfer coefficient β_{RT} are theoretically calculated from Eq. (6) and experimentally obtained β_e are summarized in Fig 1.

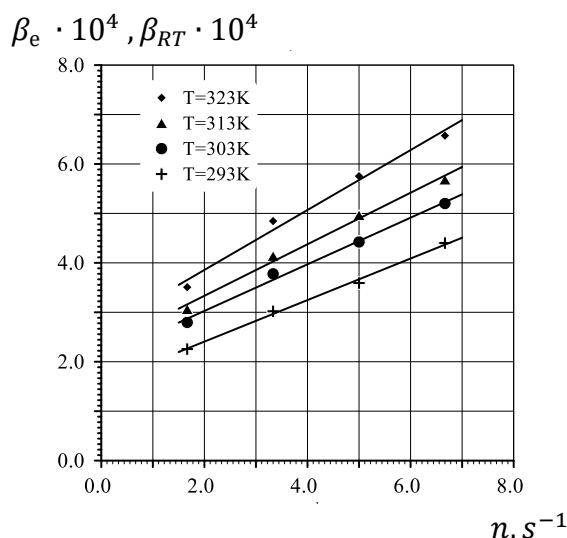


Fig. 1. Dependence of mass transfer coefficients β_e and on the stirring frequency and the temperature of the solvent β_{RT} .

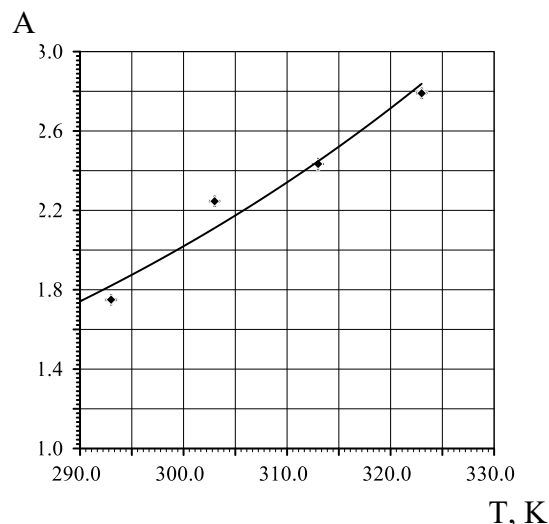


Fig. 2. Dependence of the approximation coefficient A on the temperature of the solvent T .

The dependence of the mass transfer coefficient on the stirring frequency of the agitator and temperature can generally be represented as:

$$\beta_{nT} = f(n, T) \quad (11)$$

In order to determine the effect of temperature on the mass transfer coefficient, the results of the experiments were presented in the form of a graphical dependence of Fig. 2 and approximating them by exponential dependence, we obtained the dependence of the coefficient A on temperature.

Then, to predict the process of dissolution of ATFB balls depending on the temperature of the solvent and the stirring frequency, the following calculated dependence was obtained:

$$\beta_{nT} = 2.2 \cdot 10^{-6} \cdot \exp(0.015 \cdot T) \cdot n^{0.45} \quad (12)$$

Using Eq. (12) and experimentally obtained results, the dependence of the mass transfer coefficient β_{nT} and the experimentally obtained coefficient β_e on the stirring frequency is presented in Fig. 3.

Fig. 4 shows the deviation of the obtained values β_{nT} according to Eq. (12) from the theoretically calculated value β_{RT} according to Eq. (6).

The absolute value of the relative error of the deviation of the experimentally obtained values of the mass transfer coefficient from the theoretically calculated values according to Eqs. (6) and (12) is less than 5%, which is the permissible error for mass transfer processes in chemical, pharmaceutical and food industries.

It should be noted that Eq. (12) is much easier to use in production than Eq. (6), and the absolute error between the obtained values of dependencies is acceptable.

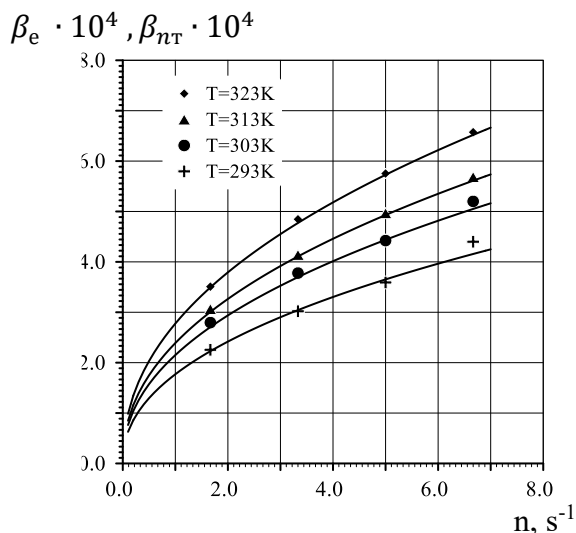


Fig.3. Dependence of mass transfer coefficients β_e and β_{nt} on the stirring frequency and the temperature of the solvent

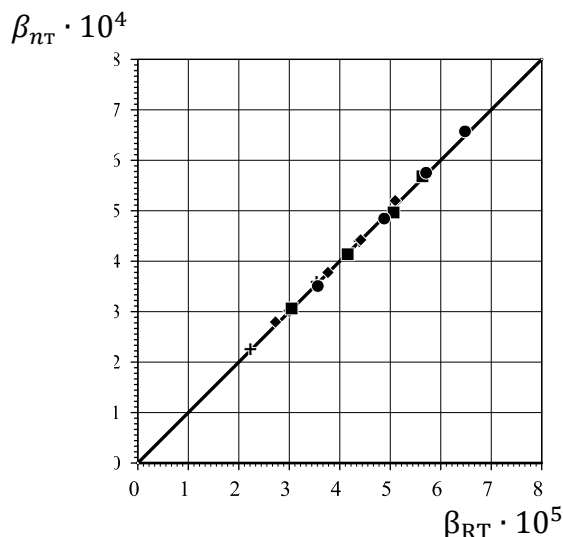


Fig.4. Deviation of the obtained values β_{nt} according to Eq. (12) from theoretically calculated β_{RT} according to Eq. (6)

Conclusions

The kinetics of dissolution of ATFB, depending on the temperature of the solution and the stirring frequency, were investigated. Mass transfer coefficients have been experimentally determined and compared with theoretically determined ones (Fig. 1,3).

A computational dependence (12) has been obtained, which makes it possible to predict the process of dissolution of ATFB depending on the temperature of the solution and the stirring frequency.

The obtained results confirm the significant influence of reactor design parameters and mixing conditions on the mass transfer process in the solid-liquid system. In general, the obtained results of the study make it possible to simulate and optimize the processes of mass transfer in solid-liquid systems, which in turn makes it possible to further optimize technological processes in the chemical industry and ensure a reduction in the energy consumption of the dissolution process.

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Pressure Influence on the Carbon Gasification Process

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Abstract. *This paper provides a theoretical analysis of the pressure influence on the carbon gasification process. It has been determined that with increasing pressure, gas yield and its energy value decrease. The obtained theoretical results will serve as a basis for future experimental research and the development of scientific-practical approaches to the complex processing of industrial and household waste.*

Keywords: carbon gasification, pyrolysis, solid waste, syngas, heat of combustion.

Introduction

A promising method for processing low-calorie fuel and recycling industrial/household solid waste is pyrolysis. Pyrolysis is a high-temperature decomposition of organic substances (oil products, coal, peat, wood, industrial/household waste, etc.) in an oxygen-free environment, or with minimal oxygen presence. From a practical point of view, it is advisable to consider low-temperature pyrolysis – a thermal decomposition of organic materials without air access – at temperatures of 450-550°C. The result is a solid residue, mainly carbon, and by-products: pyrolysis gas and liquid phase, the composition of which depends on the characteristics of the feedstock.

The main advantages of pyrolysis technologies: neutralization of toxic compounds, reduction of landfill volumes and gas emissions into the environment, as well as production of valuable products (liquid and gaseous hydrocarbons, carbon black, etc.) [1-4].

Previous studies [5-7] substantiated the feasibility of pyrolysis waste treatment. In particular, it was shown that it is economically feasible and technologically possible to use a two-stage pyrolysis decomposition method for processing wooden railway sleepers and large-tonnage coal mining waste. The first stage should be conducted in the temperature range of 200 to 450°C (low-temperature pyrolysis), and the second stage (gasification of the formed coal) – at high temperatures of 600-1000°C. The high-temperature gasification of coal with water vapor produces syngas (the main components are carbon monoxide (CO) and hydrogen (H₂), which is used for the synthesis of hydrocarbons or as an efficient fuel in electricity generation. The use of two-stage schemes increases the economic efficiency and environmental friendliness of the technology.

Low-temperature pyrolysis is an exothermic process, and therefore occurs almost completely in the specified temperature range. The second stage (high-temperature coal gasification) is based on endothermic processes, therefore, to ensure the autothermicity of the process, thermodynamic calculations were performed [6], on the basis of which the equilibrium constants of all the main gasification process reactions were calculated, and the technologically feasible temperature range for the conversion process was determined. Also, theoretical research was conducted on the influence of temperature and pressure on the specific volume of syngas formed during carbon gasification [7]. In [8], the equilibrium compositions and volumes of carbon conversion gases were calculated depending on the process temperature.

Pressure in the reaction system exerts a significant influence on the processes occurring in the gas phase, so the **purpose of this research** is to determine the influence of the pressure in the system on the qualitative composition and volume of carbon conversion gases with water vapor.

Research materials and methods

The key process parameters were determined to perform the calculations, in particular temperature, pressure, and value of the equilibrium constant for the chemical reaction under the specified conditions. To determine the equilibrium composition of a mixture, it is necessary to calculate the concentrations of initial substances and reaction products in a state of equilibrium. The calculation method is based on the law of acting masses, which allows determining the equilibrium concentrations of the reaction system components. The equilibrium constant K_p for a particular reaction is calculated by the corresponding equation (1), while inert gases and impurities that are not involved in the chemical process are not taken into account.

$$K_p = \frac{p_R^r \cdot p_S^s}{p_A^a \cdot p_B^b}, \quad (1)$$

where p_R, p_S, p_A, p_B – are equilibrium partial pressures of reaction products and initial substances, respectively; a, b, r, s – are stoichiometric coefficients in the reaction equation.

Thus, the main purpose of calculation is to solve the equilibrium equations taking into account the specified parameters, which allows predicting the composition of the gas mixture at the final stage of the process.

According to Dalton's law, the total pressure of a mixture of ideal gases is equal to the sum of the partial pressures of each gas included in this mixture:

$$p_i = N_i P = \frac{n_i}{\sum n_i} P. \quad (2)$$

Substituting (2) into (1), we obtain:

$$K_p = \frac{N_R^r N_S^s}{N_A^a N_B^b} P^{\Delta \nu}, \quad (3)$$

where N_i – is the molar fraction of the i -th component;

P – is the pressure in the system;

$\Delta \nu$ – is the sum of stoichiometric coefficients in reaction equation ($\Delta \nu = r + s - a - b$).

Using a stoichiometric equation, a functional dependence was determined between the reacted amount of an arbitrarily selected component and the reacted amounts of other reaction components.

Thus, the analysis of stoichiometry and pressure change helps to predict the composition of the gas mixture in the processes of carbon gasification and syngas production by the main reaction



The resulting gas combustion heat was determined by the lower combustion heat, which for syngas components, kJ/nm^3 , is: H_2 – 10790 and CO – 12640.

Calculations were performed in the range of pressures and temperatures: 1-10 atm and 660-960°C, respectively. All calculations are given per 1 kg of carbon.

Research results and their discussion

The results of theoretical research are presented graphically (Figs. 1-4) and in the table. With increasing pressure, the amount of gas (gas yield) and its quality (combustion heat) decrease. Particularly noticeable deterioration is observed in the temperature range of 660-860°C. This is

explained by a significant shift in the equilibrium of the reaction to the left and an increase in the water vapor share in the gas. That is, the negative influence of pressure on the equilibrium parameters of the carbon conversion process is well consistent with Le Châtelier's principle.

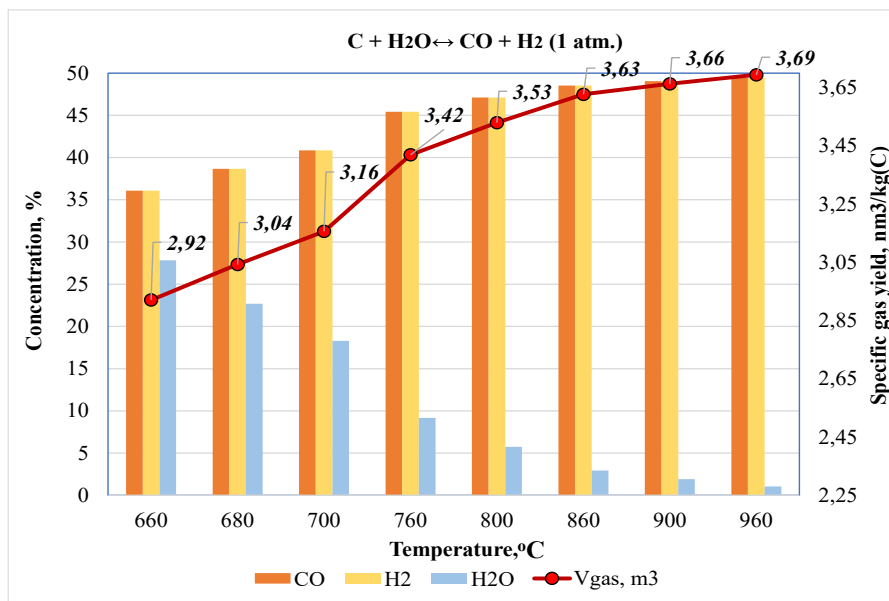


Fig. 1. Dependence of equilibrium composition and volume of gas on temperature at a pressure of 1.0 atm for the process $C + H_2O \leftrightarrow CO + H_2$.

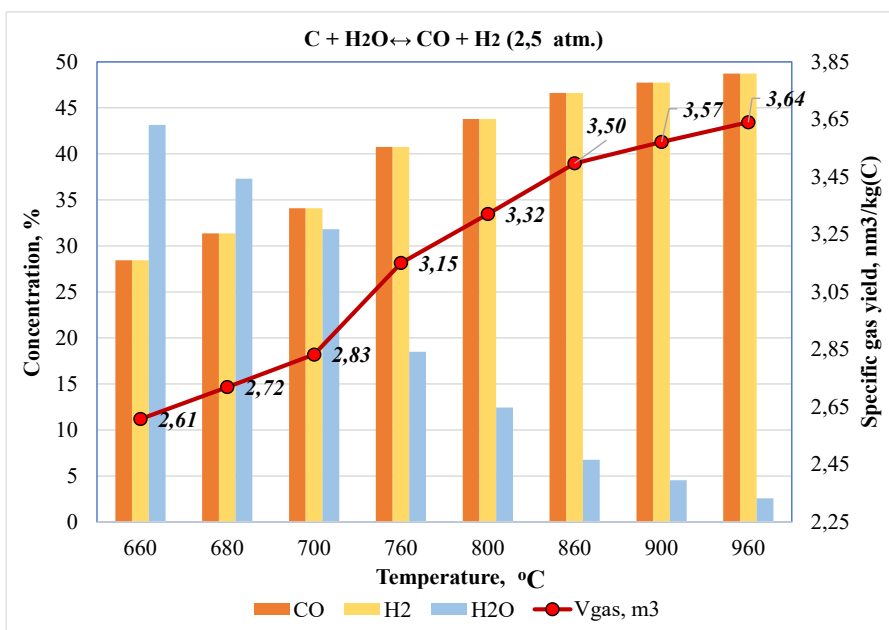


Fig. 2. Dependence of equilibrium composition and volume of gas on temperature at a pressure of 2.5 atm for the process $C + H_2O \leftrightarrow CO + H_2$.

The influence of pressure on the equilibrium constant is described by the second Van 't Hoff equation:

$$\frac{d \ln K_N}{dP} = -\frac{\Delta V}{RT}, \quad (5)$$

where ΔV — is a change in molar volume of the reaction mixture for the test system, $\Delta V > 0$.

Analysis of the equation shows:

- If the reaction is accompanied by an increase in the gas volume ($\Delta V > 0$), the derivative ($d \ln K_N / dP$) is negative, that is, the pressure increase reduces the K_N value.

- If the reaction proceeds with a decrease in gas volume ($\Delta V < 0$), the derivative is positive, hence the equilibrium constant increases with increasing pressure.

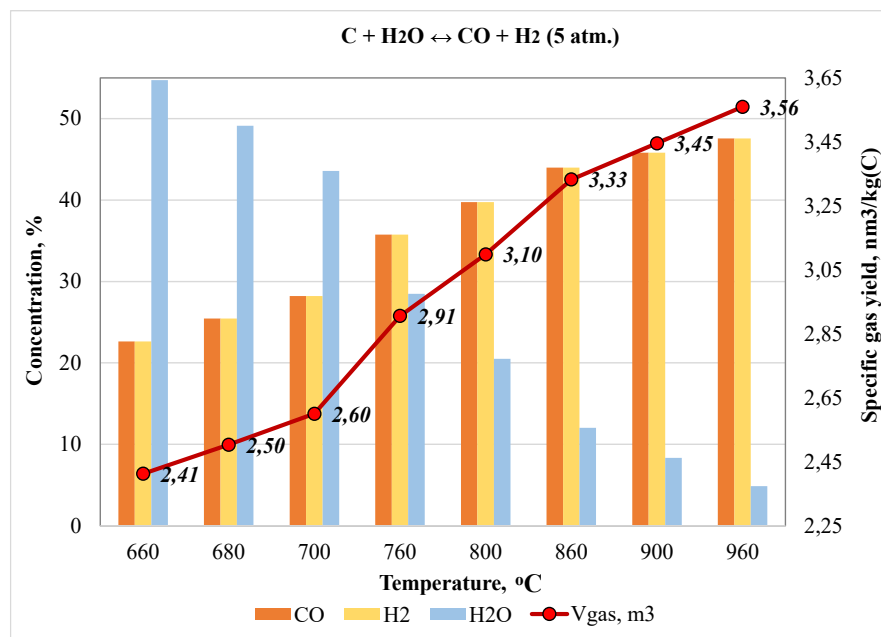


Fig. 3. Dependence of equilibrium composition and volume of gas on temperature at a pressure of 5.0 atm for the process $C + H_2O \leftrightarrow CO + H_2$.

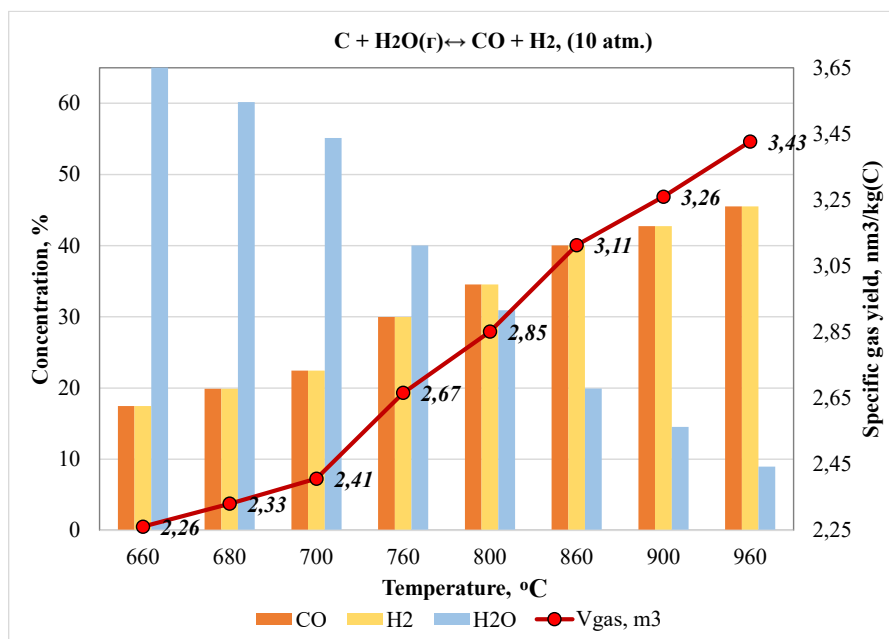


Fig. 4. Dependence of equilibrium composition and volume of gas on temperature at a pressure of 10.0 atm for the process $C + H_2O \leftrightarrow CO + H_2$.

Theoretical research is based on thermodynamic calculations, which only indicate the probability of a process, but do not determine its duration. Accordingly, it is impossible to say unequivocally that the increased pressure has a negative impact. The dependence of the degree of conversion on the time required to achieve an equilibrium state belongs to the field of chemical kinetics and requires further experimental research.

In addition to physical-chemical aspects, the industry also takes into account technical-economic factors. In particular, increased pressure makes it possible to reduce the reaction equipment sizes, which can be advantageous from an engineering and financial point of view.

Table 1

Influence of temperature and pressure on the resulting gas combustion heat

Wet gas combustion heat, kJ/nm ³								
Pressure, atm.	Temperature, °C							
	660	680	700	760	800	860	900	960
1.0	8456	9057	9573	10639	11040	11372	11491	11591
2.5	6660	7345	7988	9549	10259	10924	11184	11415
5.0	5304	5960	6610	8379	9314	10306	10736	11143
10.0	4090	4665	5257	7025	8092	9381	10012	10667

Conclusions

The technologically feasible temperature for conducting the carbon conversion process with water vapor is in the range of 860-960°C. The influence of increased pressure on the equilibrium degree of carbon conversion is ambiguous: it can both reduce it and intensify the process rate. Due to the influence of numerous factors, such as carbon size and porosity, an accurate theoretical calculation of the coal gasification rate is difficult. For this reason, it is necessary to conduct experimental research, the results of which will be published in subsequent publications.

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QM/MM Study of the Cyclization Reaction Mechanism for Pimelic o-Aminobenzamide Histone Deacetylase (HDAC) Inhibitor 4b

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Abstract. *The detailed mechanism of the intramolecular cyclization reaction of pimelic o-aminobenzamide histone deacetylase (HDAC) inhibitor 4b (N¹-(2-aminophenyl)-N⁷-phenylheptanediamide) was studied using Molecular Dynamics (MD) simulations for conformational sampling and a hybrid Quantum Mechanical/Molecular Mechanical (QM/MM) method for the energy profiling during the reaction progress, as well as for verifying the topology of the intermediates.*

Keywords: Histone deacetylase, histone deacetylase inhibitors, 2-aminobenzamide, QM/MM, MD simulations, reaction mechanisms, intramolecular cyclization

Introduction

Histone deacetylases (HDACs) are a family of epigenetic proteins that regulate gene transcription and influence various cellular processes, including proliferation, differentiation, migration, apoptosis, and angiogenesis [1]. The expression levels of HDACs are generally higher in tumor cells than in normal cells. HDAC inhibition can lead to diverse effects on cellular signaling and transcription, including cell death, differentiation, autophagy, and increased immunogenicity [2]. That is why histone deacetylase inhibitors (HDACi) hold significant potential as therapeutic agents for cancer treatment and have demonstrated notable anticancer efficacy across a range of cancers, most impressively in hematological malignancies [3].

HDACi in general are known to elevate acetylation of histones, resulting in a more relaxed chromatin structure that facilitates gene transcription [4]. There is growing evidence that many HDACs, including class I HDACs, are capable of deacetylating non-histone proteins [5], potentially contributing to their beneficial effects. Based on some microarray studies, it has been shown that HDACi can lead to both the upregulation and downregulation of gene expression patterns [6]. This suggests that HDAC inhibition may influence the expression of other regulatory enzymes and/or cofactors, which then function as activators or repressors of gene activity. HDAC inhibition was reported to alter the expression of several DNA methylation-related genes and, further, that HDAC inhibition could induce DNA methylation changes on a genome-wide scale [7].

Class I-specific, benzamide-type HDAC inhibitors have gained renewed interest in recent years due to their effectiveness in improving phenotypes in cell and mouse models of Friedreich's ataxia (FRDA) and Huntington's disease (HD) [8]. Highly active HDAC1/3-targeting inhibitor, HDACi **4b** (N¹-(2-aminophenyl)-N⁷-phenylheptanediamide) was shown to act on FRDA primary lymphocytes to significantly enhance acetylation of histone tail lysines, H3K14, H4K5, and

H4K12 in the FXN gene, leading to a significant increase in FXN mRNA levels [9]. Human cells from FRDA patients treated with HDACi **4b** resulted in a substantial increase in frataxin, accompanied by increased histone H3 acetylation near the GAA repeat [10].

The evaluation of the pharmacology, ADME, and pharmacokinetic properties of HDACi **4b** in mice was reported, aimed to assess the suitability of **4b** for translation into clinical trials [11]. The reported procedure of **4b** purification by preparative HPLC with trifluoroacetate (TFA) in the eluent suggested that **4b** had been most likely isolated as its TFA salt [9]. The study of **4b** TFA salt stability led to the observation that it cyclised slowly when left in solution to a benzimidazole product at ambient temperature and more rapidly when heated. This purified cyclized product was readily soluble in aqueous media. However, profiling against the biochemical and cellular HDAC assays determined that it retained no activity against any HDACs.

In the present paper, we propose a possible mechanism for the intramolecular cyclization reaction of N^1 -(2-aminophenyl)- N^7 -phenylheptanediamide **4b** and carry out its computational study through Molecular dynamics (MD) simulation and hybrid Quantum Mechanics/Molecular Mechanics (QM/MM) calculations. We have performed a comprehensive and sequential study of the reaction mechanism starting with the characterization of the dynamic behaviour of HDACi **4b** in a customized mixed solvent environment, followed by the energy profiling during the reaction proceeding and the topology verification of the key intermediates.

Materials and methods

The structure of the benzenaminium ion of compound **4b** was built in ChemDraw. A three-dimensional model of the compound was generated using the LigPrep module of Schrödinger software [12]. Input chiralities were retained, protonation states were generated with Epik at pH 2.0, and the resulting structures were optimized using the Optimized Potentials for Liquid Simulations-2005 OPLS2005 force-field.

The geometry of compound **4b** was optimized using Gaussian09 [13] with the HF level of theory using a 6-31G** basis set, and the charge distribution was calculated. The force field parameters for the input structure were produced using a generalized AMBER force field (GAFF) in the antechamber module [14] of the Amber 22 suite [15]. The associated partial atomic charges were also generated by applying the restraint electrostatic potential (RESP) method of QM calculated charges at the HF/6-31G** level of theory. The TFA molecule was prepared and parametrized using the same protocol. Subsequently, the tLEaP tool was used to generate topology parameters for the molecules and coordinate input files.

Solvation of compound **4b** in mixed solvent environment was performed through the customized solvent box generation using PACKMOL webserver (<https://m3g.github.io/packmol/>). In order to construct mixed solvent consisting of water and TFA at 1% v/v, the coordinates of each type of molecule (**4b**, TIP3P water and TFA) were provided in pdb format, which allowed PACKMOL to construct the customer solvent boxes by packing one **4b** ion, 3826 water molecules and 30 TFA molecules inside the rectangular cube with all sides' length of 50 Å. The tolerance was specified as 2.0 Å, which ensured the distance between atoms of different molecules was greater than that value. Finally, the pdb file for the whole solvated system was generated.

The system was then neutralized with the tLEaP program by adding counter-ions at the points of lowest electrostatic potential to reach the final net charge of 0. As TFA molecules were completely ionized at pH=2.0 (strongest acidic $pK_a = 0.05$), while **4b** ion contained a protonated amino group and existed in the form of the cation, 29 Na^+ ions were added to the system by replacing random water molecules with ions. Finally, Amber topology and coordinate files were generated for the solvated and neutralized systems.

MD simulations of the parametrized system were performed in four stages: minimization, thermalization, equilibration, and production run. Energy minimization was carried out in two steps. Firstly, a minimization run with the restrained ligand position was performed. A total of 50000 cycles of minimization were conducted, initiated by 300 steps of steepest descent minimization, followed by running 49700 steps using the conjugate gradient method. The second step was the global minimization, which ensured the entire system minimized without the positional restraints. 50000 steps of minimization were run, after 2000 cycles minimization method was switched from steepest descent to conjugate gradient. Both minimizations were run at constant volume, and a 10.0 Å cut-off was applied to non-bound electrostatic interactions. After minimization, the system was heated with the restraint on the solute position. The temperature was raised from 100 to 300 K through linear heating with the MD simulation at constant volume. Heating was fulfilled in 300000 steps (1 fs step size) with a collision frequency of 1.0 ps⁻¹. Temperature control was ensured with the Langevin dynamics thermostat during the 300 ps simulation. Next, the system was equilibrated. The restraints were switched off, and the equilibration was performed during 300 ps, or 300000 steps (1 fs step time). The system was coupled simultaneously to a thermostat at 300 K and a barostat at 1 atm with a relaxation time of 2 ps, the NPT (constant Number of particles, Pressure, and Temperature) simulation was performed to allow the density of the system to reach its equilibrium value. Production 20 ns dynamics was then performed using the isobaric-isothermal NPT ensemble with a 2-fs time step, and coordinates were saved every 20 ps for analysis. SHAKE algorithm [16, 17] was implemented to restrain the motion of hydrogen-containing bonds, Particle Mesh Ewald (PME) was used for long-range electrostatic interactions, and the cut-off radius for Lennard-Jones interactions was set to 10 Å. The MD trajectory was generated by 1000 snapshots collected, and the cpptraj module [18] of Amber 22 was used to calculate the root mean square deviation (RMSD) of the atomic positions of the ligand and to monitor its structural parameters.

Steered MD (SMD) calculations were performed on the representative snapshot 109 taken from the MD simulation trajectory. According to the QM/MM approach [19], the solvated system was split into two subsystems: the QM and MM regions. The **4b** ion was considered as the QM region, with its electrostatic and van der Waals effects accounted for by QM calculations. The QM optimizations were performed using the DFTB3 [20, 21] Hamiltonian. For the MM layer, which consisted of the mixed solvent molecules, the Amber GAFF and TIP3P force fields were utilized for TFA and water molecules, respectively. Periodic boundary conditions with the smooth particle mesh Ewald (SPME) method were used for nonbonded interactions, with a cutoff of 9 Å. The temperature of 300 K was controlled using the weak-coupling algorithm. The two systems were equilibrated without any constraints for 20 ps using an integration time step of 0.1 fs. Simulations were performed with the Sander program within the AMBER 22 suite.

Results and Discussion

Beconi *et al.* [11] evaluated of cellular activity and ADME properties of the HDAC subtype HDAC1/3-targeting inhibitor, HDACi **4b**. They reported the physicochemical instability of the acidic salts of **4b** and disclosed the conversion of the parent compound into the inactive benzimidazole **C1** (Fig. 1). Degradation of **4b** to **C1** was observed under acidic conditions at ambient temperature and occurred more rapidly when heated. Cellular HDAC assays confirmed that **C1** was expectedly inactive against HDACs, as its benzamide functionality required for chelation with zinc ion in the HDAC catalytic site, was involved in cyclisation with the ortho-amino moiety.

The cyclization of an aminophenyl moiety and amide functionality in the ortho position can occur through an intramolecular nucleophilic attack, leading to the formation of a fused heterocyclic system. This mechanism is commonly observed in the synthesis of benzimidazoles, quinazolines, and related heterocycles [22, 23].

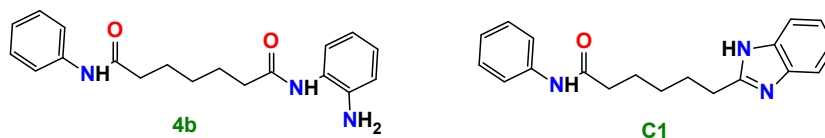


Fig. 1. Chemical structure of the HDACi **4b** molecule and the benzimidazole product of its cyclization **C1**.

In the present study, we propose the intramolecular cyclization mechanism for N^1 -(2-aminophenyl)- N^7 -phenylheptanediamide (compound **4b**) that proceeds through four steps (Fig. 2). We begin with the benzenaminium ion of compound **4b**, as its ortho-amino group is protonated in the acidic environment at pH of 2.0.

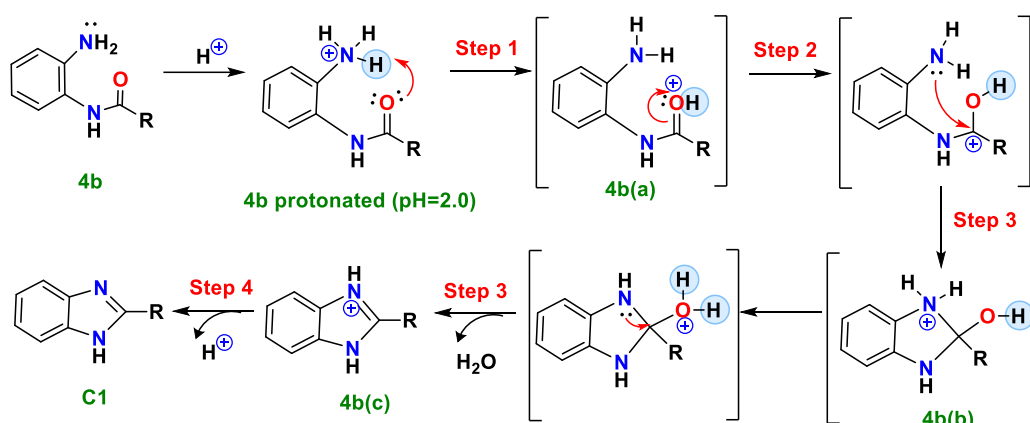


Fig. 2. Proposed intramolecular cyclization mechanism for HDACi **4b**.

The main steps of the proposed cyclization mechanism include:

Step 1. Protonation of the amide functionality. The amide carbonyl Oxygen is protonated under acidic conditions (intermediate **4b(a)**). This increases the electrophilicity of the carbonyl carbon and activates it for nucleophilic attack.

Step 2. Nucleophilic attack by the ortho-amino group. The ortho-amino group acts as a nucleophile and attacks the activated amide carbonyl carbon, leading to the formation of a tetrahedral intermediate **4b(b)**.

Step 3. Cyclization and water loss. The previous stage intermediate undergoes dehydration, leading to the formation of a cyclic imine structure **4b(c)**.

Step 4. Aromatization. Under acidic conditions, the imine undergoes tautomerization with a proton elimination to yield benzimidazolone **C1**, stabilizing the final fully conjugated heterocyclic structure.

We used MD simulations for the conformational sampling of HDACi **4b** in the equilibrated mixed solvent, and hybrid QM/MM calculations for exploring the cyclization reaction mechanism.

To explore the conformational behavior of **4b** in a mixed water-TFA (1% v/v) environment, the appropriate protonation state of the compound was assigned at pH 2.0. Solvation in the mixed solvent environment was achieved using a customized solvent box generated with the PACKMOL web server (<https://m3g.github.io/packmol/>). The conformational search workflow involved geometry optimization of **4b** using Gaussian09, followed by MD simulations with the Amber 22

suite. The MD production run was conducted for 20 ns, with snapshots collected every 20 ps, yielding a total of 200 snapshots. Trajectory analysis was performed using the cpptraj module.

The system's density was monitored during NPT equilibration to ensure that it reached a stable value. The equilibration stage simulations resulted in an average system density of 1.0215 g/cm³ (Fig. 3).

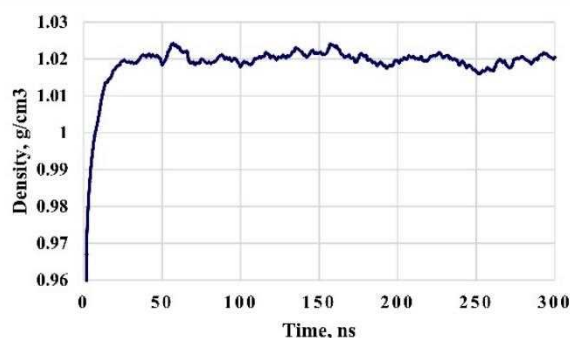


Fig. 3. System density as a function of time during the NPT equilibration stage of the MD simulation.

The computed RMSD values for the atomic positions of HDACi **4b**, relative to its equilibrated structure during the MD simulation, ranged from 0.80 to 3.54 Å, with an average of 2.457 Å (Fig. 4a). The structural parameters of **4b** were also recorded throughout the MD simulation. The interatomic distance between the nitrogen atom of the aminophenyl moiety and the carbon atom of the amide functionality (**Dist_NH₂-C(O)**, Fig. 4b) and the dihedral angle between the aminophenyl group and the amide functionality planes (**Dihedral C1-C6-N2-C7**, Fig. 4c) were monitored. It can be concluded that fluctuations in the RMSD trajectory were caused by some conformational changes or structural rearrangements of the **4b** ion, particularly those related to **Dihedral C1-C6-N2-C7** fluctuations.

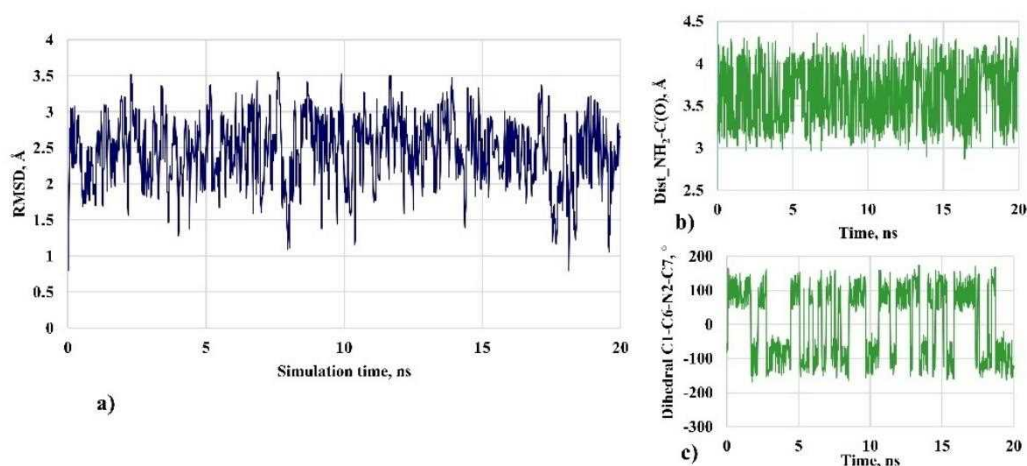


Fig. 4. a) RMSD of **4b** atomic positions as a function of time during the MD productive phase (20 ns). Variations in (b) interatomic distance between nitrogen atom of aminophenyl moiety and carbon atom of amide functionality **Dist_NH₂-C(O)** and (c) dihedral angle between amino phenyl group and amide functionality planes **Dihedral C1-C6-N2-C7** throughout the MD productive phase.

MD trajectory was analysed with respect to cyclization possibility. The selection criteria were fixed as: **Dist_NH₂-C(O)** < 3.3 Å, **Dihedral C1-C6-N2-C7** = -40° ÷ 40°. This filtering

allowed us to retrieve 15 snapshots from the whole MD trajectory, which satisfied the above-mentioned criteria. Finally, frame 109 was selected for further analysis after visually inspecting the pre-selected snapshots (Fig. 5).

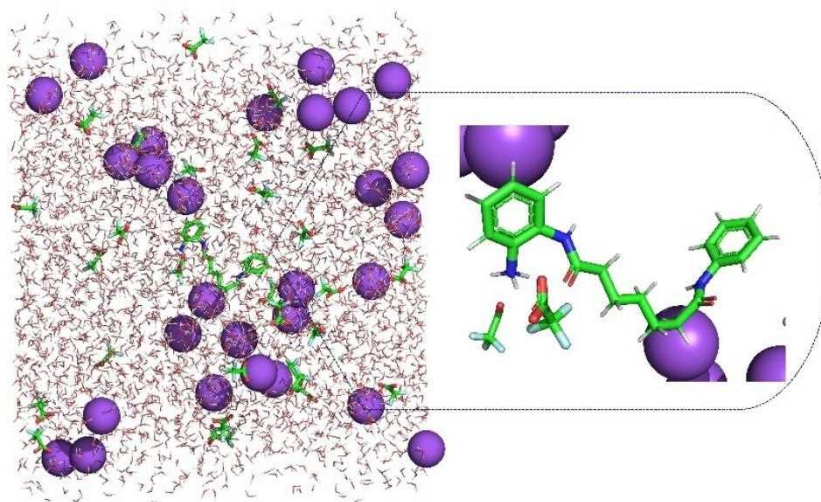


Fig 5. Architecture of the customized mixed solvated system and **4b** benzenaminium ion conformation corresponding to snapshot 109 of the classical MD production step

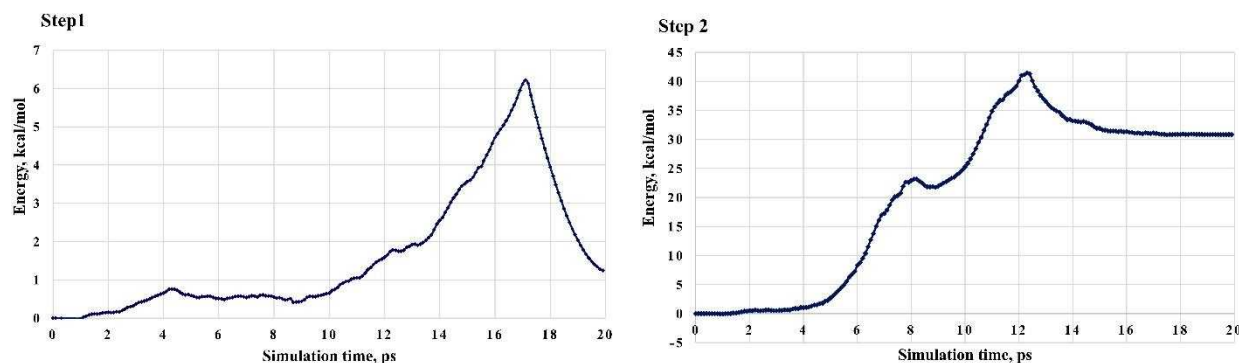
As observed, the orientation of **4b** before the QM(DFTB3)/MM MD equilibration was suitable for both protonation of the amide carbonyl Oxygen by the benzenaminium moiety and the nucleophilic attack of the carbonyl functionality Carbon by the ortho-amino group.

A combination of SMD and QM/MM techniques was employed to investigate the cyclization reaction mechanism, using MD snapshot 109 as the starting point. The solvated system was split into two subsystems: the QM region, consisting of **4b** ion, which was treated by QM methods at DFTB3 level of theory, and the MM region, consisting of the mixed solvent molecules, which was treated with MM methods with the Amber GAFF and TIP3P force fields utilization. The two systems were simulated without any constraints for 20 ps.

For the Step 1 of the proposed reaction mechanism (protonation of the carbonyl oxygen of the amide moiety) the “Distance” approach of the QM calculations was applied. This approach supposed that the distance between the hydrogen atom of the benzenaminium moiety and the amide carbonyl oxygen atom was decreased linearly in the range from 2.4 Å to 1.0 Å. Steps 2 and 3 of the reaction mechanism, namely the nucleophilic intramolecular attack of the amide carbonyl carbon by the nitrogen atom of ortho-amino group, followed by cyclization, resulted in cyclic imine structure formation, and water loss, were combined into a single Step 2 of the QM calculations using the “Linear combination of distances (LCOD)” approach. Under this approach, we decreased the distance between the amino group nitrogen and the amide carbon in the range from 3.5 Å to 1.3 Å and increased the distance between the amide carbon and the carbonyl oxygen from 1.3 Å to 3.5 Å simultaneously.

The analysis of the obtained energy profiles indicated that during Step 1, the energy of the system gradually increased with small fluctuations (Fig. 6). About 16-18 ps, there was a sharp peak, after which the energy began to decrease. This may indicate overcoming the energy barrier and the transition of the system to a new state. The transfer of a hydrogen atom from the benzenaminium moiety to the amide carbonyl Oxygen atom had an energetic barrier of 6.22 kcal/mol; the total work done was 1.21 kcal/mol. On Step 2, energy increased more rapidly starting from 4 ps, which may indicate the activation of the reaction. There were two significant peaks (around 8 ps and 12

ps), which may correspond to the intermediate states or transitional structures. After 12 ps of the simulation, the energy gradually decreased and stabilized, which may indicate the formation of the



reaction product. This step had a higher barrier of 41.45 kcal/mol, with the total work of the transformation done of 30.84 kcal/mol.

Fig. 6. Energy profiles (in kcal·mol⁻¹) obtained from Step 1 (“Distance” approach) and Step 2 (“LCOD” approach) of QM Calculations.

The structure of the QM step 1 intermediate displayed the hydrogen atom transferring from the ortho-ammonium moiety to the amide oxygen atom (Fig.7). It can be seen that the resulting QM step 2 structure ensured cyclization with the fused imine, obtaining the N-C interatomic distance calculated as 1.3 Å. Simultaneously, the intermediate had undergone dehydration, which was ensured by the C-O distance of 3.6 Å corresponding to the water molecule loss.

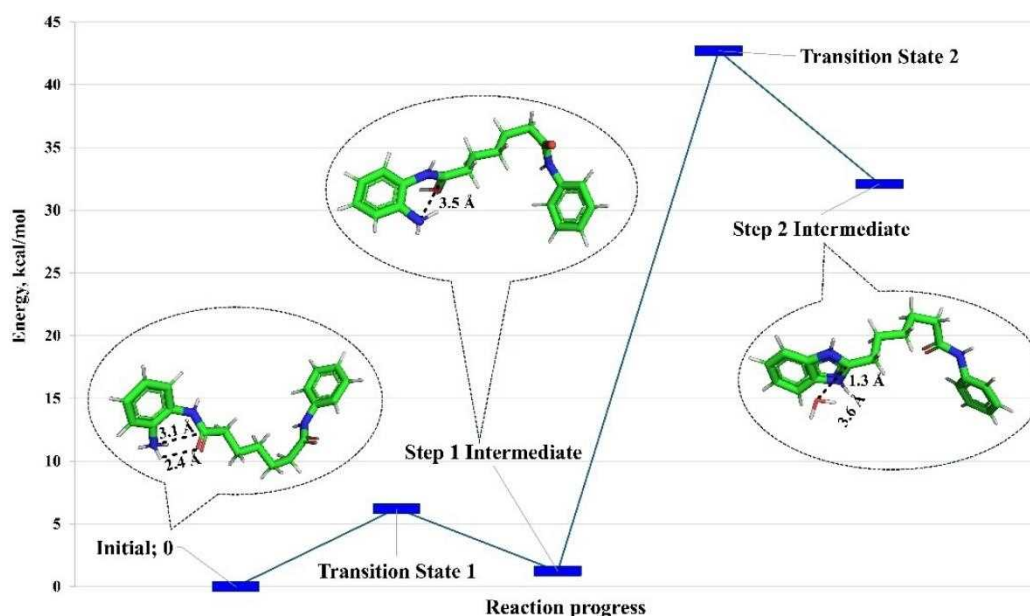


Fig 7. Schematic diagram of the energy profile, barriers for the reaction process, and representations of the intermediate structures corresponding to QM steps 1 and 2.

However, the results obtained from the MD simulations were insufficient to capture the configurational transitions across the high-energy barriers observed in the MD trajectories, due to the gap between the timescale covered by short MD simulations and the timescale required for adequate local sampling of transition state regions. To clarify the optimal geometry of the transition states and improve the energetic profile in the high-energy regions of chemical space, we suppose that it would be worthwhile to apply the umbrella sampling technique along the proposed reaction coordinate.

Conclusions

Using MD simulations and QM/MM calculations, we have studied the mechanism of intramolecular cyclization reaction for N¹-(2-aminophenyl)-N⁷-phenylheptanediamide (compound **4b**), proceeding through several steps. The results of the QM/MM modeling indicate that the reaction possibly proceeds, as energy barriers were overcome in both QM steps, and the transitions to more stable states were observed at the end of the simulations. The presence of several energy peaks suggests a complex, multi-stage reaction mechanism with intermediate states. Structural analysis of the intermediates confirmed the formation of the expected products.

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Lignocellulosic Raw Materials and Its Wastes Transformation Into Value-Added Products

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Abstract. *The aim of our work was to investigate the possibility of obtaining marketable products (fibrous and microcrystalline cellulose, cellulose acetate, lignosulfonates, oxyaldehydes, fertilizers and primings, etc.) from renewable lignocellulosic raw materials.*

Keywords: lignocellulosic raw materials, fibrous cellulose, microcrystalline cellulose, cellulose acetate, lignosulfonates, organo-mineral fertilizers, silica.

Introduction

Historically, biomass has been widely used primarily as an energy source. It is also a valuable chemical raw material for the production of almost all petrochemical synthesis products. To date, 20 basic compounds have been identified, which are sufficient for the manufacture of almost the entire range of chemical industry products and which can be obtained from plant biomass [1,2]. Ultimately, the current state of fossil fuels has emphasized the future development of the chemical industry market, which is predominantly focused on plant biomass. The attention paid in recent decades to renewables is reflected in many scientific reports [3-11].

Therefore, considering that Ukraine is an agrarian country, it is expedient to find ways to obtain marketable products from lignocellulosic raw materials and their waste.

Materials and methods

The lignocellulosic raw materials selected were its waste, as well as industrial crops, namely tree crowns (poplar, oak, birch, linden, chestnut, maple), green waste from mowing lawn grass and forbs, fallen leaves (poplar, oak, birch, linden, chestnut, maple), agricultural waste (wheat, barley, rye, oat, rapeseed, soybean straw, corn and sunflower stalks, rice husks, corn cobs) and industrial crops (giant miscanthus, sugar and Chinese miscanthus, sugar sorghum, switchgrass, flax and hemp). The contents of cellulose, hemicellulose, lignin, and other chemical components in lignocellulosic raw materials were determined by standard chemical analysis, as described earlier

[12,13]. All chemical analysis was carried out twice, allowing the calculation of the mean values and standard deviations, which do not exceed 5 %. The inorganic components were determined using Expert 3L XRF (INAM, Ukraine). The phase identification of the products was examined under X-ray diffraction (XRD) using the MiniFlex 300/600 diffractometer (Rigaku, Japan). The diffraction patterns were recorded using Cu-K α radiation ($\lambda = 0.15418$ nm), the operating voltage of 40 kV, and a current of 15 mA. The XRD pattern of the samples was obtained in the 2θ range between 2° and 80° with a step of 0.02° . FTIR analysis of the obtained products was performed using an IRAffinity-1S FTIR spectrometer (Shimadzu, Japan) equipped with a Quest ATR Diamond GS-10800X (Specac, UK) within the wavenumber range of 4000 to 400 cm^{-1} . The porous properties of the products were studied using N₂ adsorption at -195.8°C on the specific surface area and porosity analyzer Nova 1200e (Quantachrome, USA). Prior to analysis, 0.23-0.24 g of sample was degassed at 120°C for 3 h to remove previously adsorbed gases and dead space by vacuum pump to cool down the sample at room temperature. NovaWin 11.04 software was used to calculate the parameters of the porous structure, namely, the specific surface area of S_{BET} (multipoint BET method in the range of p/p_0 0.03–0.65); the specific surface area without taking into account micropores S_t and the volume of micropores V_{tmicro} - by the t-method ($V_{\alpha}\text{-}S_{\text{micro}}$ - alpha-S method), as well as the specific surface area of micropores - by the formula $S_{\text{tmicro}} = S_{\text{BET}} - S_t$; some of these parameters were also calculated by the DFT method, as was the pore size distribution using selected models. The surface morphology was investigated with an atomic force microscope (AFM) NT-206 (Company with double liability “Microtestmachines”, Belarus) equipped with a standard sonde CSC37 and rigidity of the console 0.3-0.6 N/m. The scan was run in a contact static mode at 10 $\mu\text{m/s}$ with a step of 0.3 nm. Samples (4 mg) after grinding for 10 min (only for powders) were stirred in ethyl alcohol (5 ml) for 15 min. The resulting suspension (0.25 ml) was applied to quartz glass and dried at 50°C to a constant weight. Then the scan was performed on AFM. The scanning electron microscopy (SEM) images were taken using a Zeiss Evo-10 (Carl Zeiss Microscopy, USA) microscope working at 20.0 kV. Thermogravimetric analysis (TGA) and differential scanning calorimetric analysis (DSC) were performed with a PT1600 TG-DTA/DSC (STA Simultaneous Thermal Analysis, LINSEIS Messgeräte GmbH, Germany). The samples (13.0 ± 0.1 mg) were collected in a standard corundum pan. The scan was run at 5°C/min under a flow of air. The mass change was measured from 15.8 to 100°C . The sample was analysed three times.

Results

Chemical analysis of tree crowning waste (poplar, oak, birch, linden, chestnut, maple), green waste from mowing lawn grass and forbs, fallen leaves (poplar, oak, birch, linden, chestnut, maple), agricultural waste (wheat, barley, rye, oat, rapeseed, soybean straw, corn and sunflower stalks, rice husks, corn cobs) and industrial crops (giant miscanthus, sugar and Chinese miscanthus, sugar sorghum, switchgrass, flax and hemp) was carried out. The results of the research are presented in Table 1.

It has been established that the waste is characterized by a high content of water-soluble substances and hemicelluloses, which makes them attractive for further processing by bacteria. The works [14,15] show the possibility of obtaining biobutanol from agricultural waste, switchgrass, and green waste from mowing lawn grass and forbs.

Lignocellulosic biomass with high lignin content is a promising raw material for thermolysis to biochar and activated carbon [16-19].

At the same time, technical crops are more attractive for obtaining cellulose, which is currently a pressing issue for our country. Organo-solvent cooking of flax straw, hemp, switchgrass, and

soybean straw was carried out [20-23]. The obtained cellulose materials were studied by modern physicochemical methods: low-temperature nitrogen adsorption-desorption, XRD, XRF, FTIR-ATR, AFM, SEM, TGA, and DSC. It was established that the highest yields of fibrous cellulose and MCC $\geq 90\%$ were achieved when processing technical hemp fibre of the Glesiya variety. Such products were characterized by a low content of inorganic components (0.5 and 0.2%, respectively) and lignin (1.6 and 0.8%, respectively). In terms of their physicochemical characteristics, they are not inferior to world analogues.

Table 1

Composition of lignocellulosic biomass, % mass in a.d.m.

Raw material	Ash	Pitches and fats	Water-soluble substances	Cellulose	Hemi-cellulose	Lignin	Other
Hemp hurd	2.7	0.7	3.8	48.4	25.8	20.9	0.4
Hemp fiber	1.5	0.8	5.3	85.3	6.3	2.1	0.2
Flax	5.4	1.9	8.75	48.0	27.1	14.06	0.19
Switchgrass	5.4	2.0	7.7	46.7	23.0	13.8	1.4
Wheat straw	6.5	1.2	14.5	46.5	12.9	24.6	0.3
Rye straw	6.2	1.8	7.7	46.1	15.5	28.8	0.1
Rape straw	8.0	0.9	3.0	43.7	16.7	35.5	0.2
Barley straw	7.6	1.2	7.2	50.0	24.2	17.1	0.3
Oats straw	7.1	2.1	16.1	40.2	10.0	31.2	0.4
Corn straw	9.0	1.5	19.8	36.9	11.9	29.7	0.2
Sunflower straw	14.7	2.5	16.1	27.5	10.3	43.5	0.1
Soybean straw	4.4	0.9	4.0	46.9	11.6	36.3	0.3
Rice husk	18.2	0.3	8.2	39.7	13.3	20.2	0.1
Corn cobs	1.5	0.5	4.2	43.2	26.4	23.4	0.8
Poplar branches	6.73	5.12	22.57	23.24	21.06	20.85	0.43
Oak branches	6.94	4.00	21.07	21.71	16.35	29.41	0.52
Birch branches	5.79	8.73	18.42	16.95	27.87	21.65	0.59
Linden branches	11.14	5.35	22.81	20.67	19.85	20.00	0.18
Chestnut branches	9.98	3.29	17.96	18.95	25.81	24.00	0.34
Maple branches	9.01	4.73	17.97	19.43	28.73	20.36	0.20
Poplar leaves	14.94	5.33	11.70	25.71	16.74	25.76	0.62
Oak leaves	8.44	9.82	17.61	16.77	21.88	25.30	1.01
Birch leaves	31.17	14.71	8.67	21.88	15.38	12.58	0.20
Linden leaves	18.53	5.68	4.68	25.65	24.37	21.60	0.54
Chestnut leaves	14.07	7.44	8.08	21.97	24.89	23.90	0.70
Maple leaves	13.14	9.44	10.98	19.74	31.84	14.62	0.24
Lawn grass	17.53	5.99	16.02	21.12	23.22	17.06	0.11
Roadside grass	31.63	6.00	13.76	16.88	23.23	10.25	0.15
Giant miscanthus	2.80	0.29	13.01	44.71	25.31	13.77	0.12
Sugar sorghum	8.54	0.64	30.75	31.16	19.84	9.03	0.09

From lignin, which was isolated from the cooking liquor to obtain cellulose products or after hydrolysis of the biomass itself, it is possible, in addition to carbon materials, as mentioned above, to obtain sodium and potassium lignosulfonate. The latter was used to obtain fertilizers that have successfully passed field tests [16,24]. Sodium lignosulfonate is widely used as a binder for metallurgy. In addition, lignin is a promising raw material for obtaining oxyaldehydes, as well as high-octane additives to fuels [25-27].

Based on the obtained cellulose products, cellulose acetate was obtained, which in its characteristics is similar to industrial samples, which was confirmed by the FTIR and TGA

methods. Thus, the carried out studies showed the possibility of widespread use of lignocellulosic raw materials to obtain a lot of value-added products that are currently imported from abroad.

Conclusions

Thus, we have considered possible directions for the conversion of various lignocellulosic raw materials into marketable products, which can be summarized in Fig. 1.

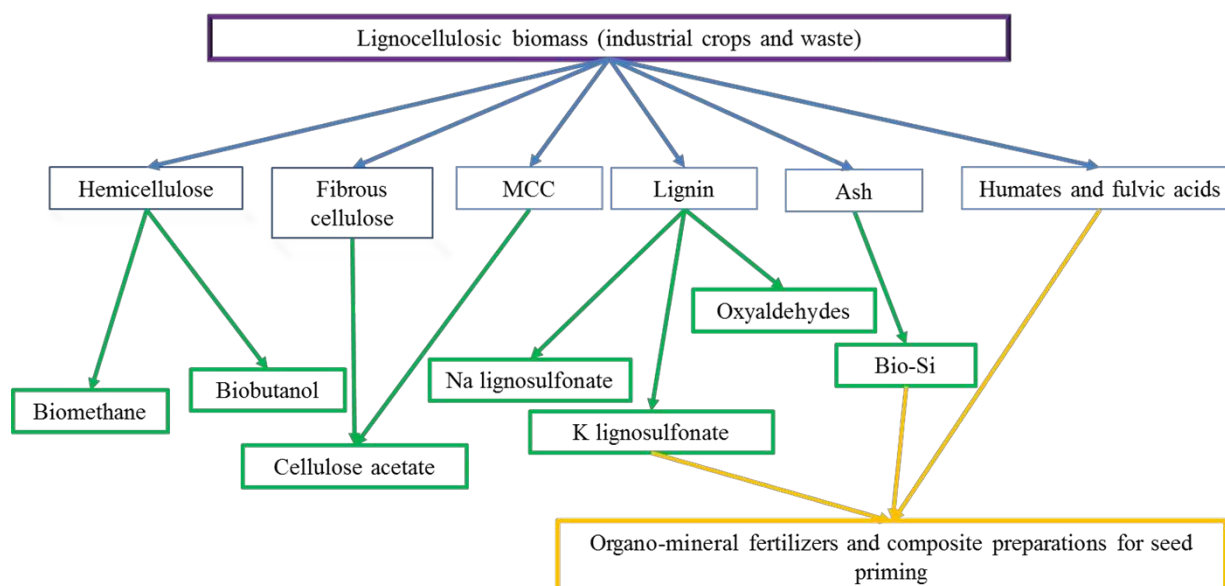


Fig. 1. Scheme of biomass processing directions.

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Diffusive Mass Transfer During Filtration Drying of Match Splints

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Abstract. *Experimental and theoretical studies of internal diffusion during filtration drying of match splints are presented. The effective coefficient of internal moisture diffusion in a stationary layer of match splints has been determined. The influence of the heat agent temperature on internal diffusion has been investigated. A dependence for determining diffusion coefficients at different temperatures has been obtained.*

Keywords: filtration drying, match splints, diffusive mass transfer, internal diffusion coefficient, stationary layer.

Introduction

Drying match splints is an important and energy-intensive process in match production. In industrial settings, match splints are dried in a belt dryer. A drawback of this method is that the heat agent flows over the surface of the material layer. Since moisture moves from the hotter surface to the cooler one, thermodiffusion occurs during such drying, which is directed opposite to the direction of moisture evaporation. As an alternative method, filtration drying in a stationary material layer has been proposed.

Filtration drying is one of the highly efficient and intensive methods of convective drying [1]. Its advantage lies in the high values of mass transfer coefficients. This is due to the large contact surface area between the phases, as the heat agent flows around all the particles. Filtration drying is conventionally divided into two periods: the period of complete saturation of the heat agent with moisture, during which the drying potential of the heat agent is the limiting stage, and the period of partial saturation of the heat agent with moisture, during which the drying rate is limited by the intensity of moisture diffusion from the inside of the material to the phase contact surface [2].

The moisture in match splints is mainly bound and located in the pores and microcapillaries. Therefore, the drying process strongly depends on the intensity of moisture diffusion from the inside of the material to the surface. To ensure the efficient use of the heat agent, the diffusion and mass transfer coefficients need to be approximately equal, which can be achieved by adjusting the velocity and temperature of the heat agent.

Therefore, an important part of the research on filtration drying of match splints is the determination of internal diffusion coefficients. The diffusion coefficient does not depend on the hydrodynamics of the heat agent but only on temperature. Thus, it is essential to investigate the influence of temperature on diffusion and to obtain dependencies for determining diffusion coefficients at different temperatures.

Materials and methods

Match splints are prismatic particles with equal width and height, and a significantly greater length.

The internal moisture diffusion in match splints was studied using an experimental setup, the operating principle of which is described in [3]. The research was conducted in a short layer. A batch of match splints with a moisture content of approximately 1.6 kg H₂O/kg of dry material was loaded into a cylindrical container.

The container was placed on the setup, and the drying agent was filtered through the layer of match splints at a constant velocity and temperatures of 313, 323, 333, 343, and 353 K. A constant temperature was maintained using a SESTOS DIS 10 electronic thermostat with an accuracy of $\pm 0.5^\circ\text{C}$. The change in the mass of the match splints was measured using Axis AD3000 electronic scales with an accuracy of ± 0.01 g. The experimental studies were carried out until the material reached a constant mass.

To describe the diffusion process, third-kind boundary conditions were used, according to which the moisture content is a function of four variables: the coordinates x, y, z , and time τ :

$$\begin{aligned} w^c(\pm R_1, y, z, \tau) &= w_{h.a}^c \\ w^c(x, \pm R_2, z, \tau) &= w_{h.a}^c, \\ w^c(x, y, \pm R_3, \tau) &= w_{h.a}^c \end{aligned} \quad (1)$$

where w^c – is the average moisture content in the material ($\text{kg H}_2\text{O/kg dry material}$) at time τ , R_1, R_2, R_3 – are characteristic dimensions in the coordinate system located at the center of the prismatic particle.

For prismatic particles, the differential equation of diffusion under third-kind boundary conditions takes the following form:

$$\frac{\partial w^c(x, y, z, \tau)}{\partial \tau} = D_w^* \left[\frac{\partial^2 w^c(x, y, z, \tau)}{\partial x^2} + \frac{\partial^2 w^c(x, y, z, \tau)}{\partial y^2} + \frac{\partial^2 w^c(x, y, z, \tau)}{\partial z^2} \right] \quad (2)$$

The solution of which can be represented as follows:

$$-\frac{\ln(\Delta W^c) - \ln(B_n B_m B_k)}{\mu^2(K_1^2 + K_2^2 + K_3^2)} = Fo \quad (3)$$

Denote:

$$A^* = -\frac{\ln(\Delta W^c) - \ln(B_n B_m B_k)}{\mu^2(K_1^2 + K_2^2 + K_3^2)} \quad (4)$$

Then, equation (4) will take the form:

$$A^* = Fo = \frac{D_w^* \tau}{R^2} \quad (5)$$

The results of the experimental studies can be presented as a graphical dependence of $A^* = f(\tau)$. By approximating the data with a linear function and using the tangent of the slope of the straight line, the internal diffusion coefficient can be determined.

Results and discussion

Based on the experimental data, a graphical dependence of moisture content on drying time $w^c = f(\tau)$ is plotted in Fig. 1.

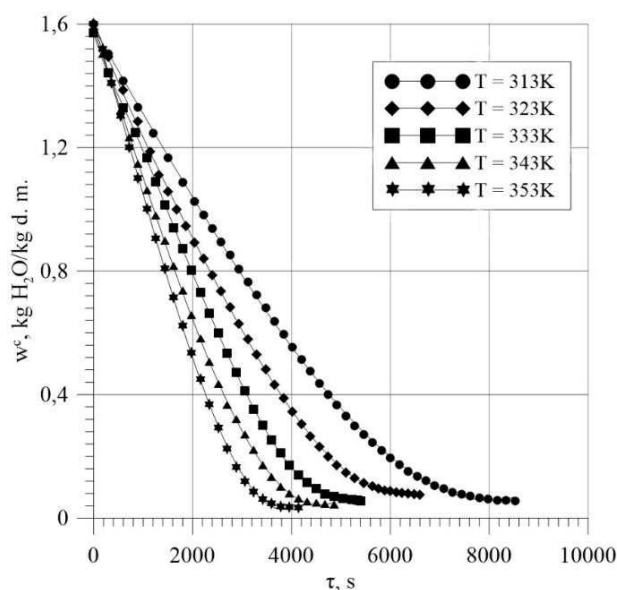


Fig.1. The graphical dependence of moisture content on drying time of match splints.

As shown by the analysis of Figure 1, with an increase in drying temperature, the drying process becomes more intensive, and the drying duration decreases. This is explained by the increase in the drying potential of the heat agent, which accelerates the drying process during the period of full moisture saturation, and the increase in the moisture diffusion rate within the material, which is important during the period of partial moisture saturation.

Based on the obtained moisture content values, the coefficient A^* was determined, and the dependence $A^* = f(\tau)$ was constructed, as shown in Fig. 2. The analysis of the figure reveals that the dependence is linear, meaning that the value of the internal diffusion coefficient can be determined by approximating the data with a linear function using the tangent of the slope angle of the straight line.

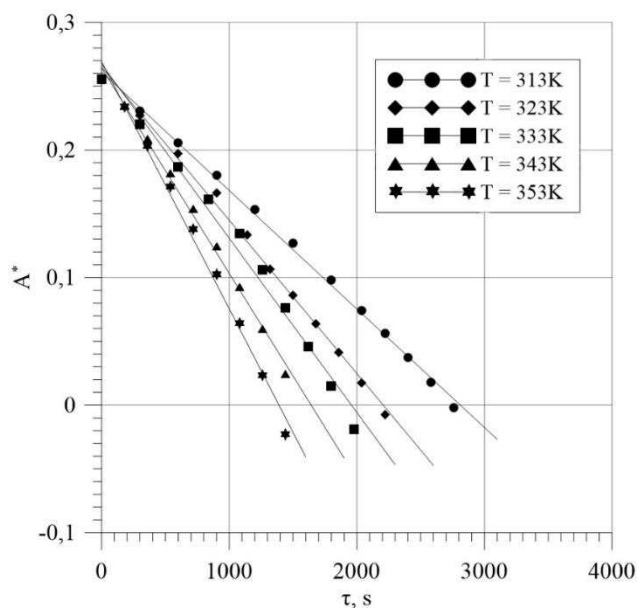


Fig.2. The graphical dependence of A^* on the drying time of match splints.

Table 1 presents the values of the diffusion coefficient in match splints within the range of 313–353 K.

Table 1

Values of the diffusion coefficient for match splints at different temperatures

T, K	293	313	323	333	343	353
$D_w^* \cdot 10^{11}, \text{m}^2/\text{s}$	2.84	6.02	7.78	8.84	10.42	12.55

As seen in Table 1, with an increase in temperature, the internal diffusion coefficient increases. The rise in the temperature of the heat agent causes an increase in the temperature inside the match splints, which contributes to the increased movement of moisture molecules within the material. Figure 3 shows the graphical dependence of the internal diffusion coefficient on temperature.

As seen in Fig. 3, the dependence $D_w = f(T)$ is linear, and therefore, it can be represented by the following calculated equation:

$$D_w^t = D_w^{293} + 1.55 \cdot 10^{-12} \cdot (T - 293) \quad (6)$$

The obtained analytical Eq. (6) allows for the theoretical determination of the internal diffusion coefficient for match splints within the temperature range of 293–353 K.

The maximum error between the experimental data and the theoretically calculated values of the internal diffusion coefficients for match splints does not exceed 3.8%.

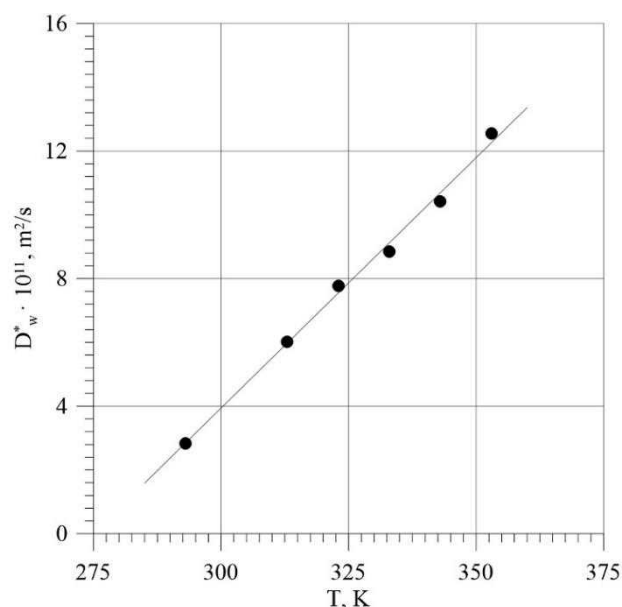


Fig.3. Graphical dependence of the internal diffusion coefficient on temperature for match splints.

Conclusions

The paper presents the results of experimental studies on internal moisture diffusion during the filtration drying of match splints. The internal diffusion coefficients at different temperatures were determined. It was shown that as the temperature increases, the diffusion coefficient also increases. A linear dependence was obtained, which allows for the determination of the diffusion coefficient during the filtration drying of match splints. The obtained dependence demonstrates high convergence with the experimental data within the temperature range of 313-353 K. The maximum error does not exceed 3.8%.

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Evaluation of the Effect of Technical Lignin on the Properties of Petroleum Bitumen

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Abstract. *The effect of technical lignin on the properties of petroleum bitumen was evaluated. The lignin sample was purified by sieving. After that, its effect on the properties of road bitumen was evaluated. The study concluded that it is advisable to use lignin as a relatively cheap substitute for petroleum bitumen.*

Keywords: hydrocarbon raw materials, technical lignin, lignocellulosic biomass, petroleum bitumen, modification.

Introduction

As is known, lignin is a complex aromatic polymer that forms part of terrestrial vascular plants. It performs a structural function, providing mechanical strength, rigidity, and hydrophobicity to plant cell walls, contributing to their resistance to biotic and abiotic environmental factors. Today, it is a rather underestimated and yet widespread material characterized by quite substantial reserves, which are renewable, and used in many industries.

The lignin content varies significantly depending on the botanical origin of the plant material. In hardwoods, including fallen leaves, branches, and bark, the lignin mass fraction ranges from 20 wt. % to 30 wt.%. In perennial herbaceous plants, such as straw and hay, the lignin content varies between 15 wt.% and 25 wt.%. Softwood species may contain up to 38 wt. % lignin by mass. The exact quantitative indicators depend on the type of plant material, growth conditions, and the method of raw material preparation.

Industrial lignin production is primarily carried out through the chemical degradation of plant material using various reagents, such as sodium sulfate, sulfuric acid, or other chemical agents, under controlled temperature conditions and processing duration [1]. As a result of such processing, lignin is obtained as a by-product. Lignin has several advantageous characteristics, including antioxidant and antibacterial properties, biodegradable and compatible properties, outstanding thermal reactivity, and adhesive capabilities. It is used in various industries, including biofuel production, chemical reagents, granular activated carbon, porous construction materials, fertilizers, acetic and oxalic acids, as well as fillers for polymer composites.

Each of the forms of lignin produced in the industry has certain characteristics that differ depending on the method of its production. Thus, hydrolyzed lignin has low solubility, reactivity, and high viscosity, which limit its use in water-based applications. At the same time, hydrolysis lignin has been used as an adhesive, flocculant, dispersant, and fire retardant. Also, hydrolysis lignin can be used in road construction as a modifier of asphalt concrete mixtures or as a raw material for the synthesis of lignin-based binding substances [2-6].

Given the aforementioned information, it was proposed to evaluate the effect of technical lignin of Ukrainian origin on the properties of petroleum bitumen for its further use in road construction.

Experimental

The lignin sample was collected at its storage site (Zaporizhzhia region, Ukraine). The lignin originated from the processing of plant material at ethanol production plants. The studied lignin was classified as «technical» due to the significant content of various mechanical impurities, primarily unprocessed plant material (Fig. 1A). Therefore, the first stage of the work involved the preparation of lignin. Its working sample was cleaned of mechanical impurities and classified using sieves. The obtained fraction ≤ 0.14 mm was then dried to an air-dry state. As a result, an analytical sample of lignin was obtained (Fig. 1B), which was used for bitumen modification. Characteristics of technical lignin are given in Table 1.



Fig. 1. Technical lignin

A – collected from the storage site; B – after cleaning from mechanical impurities and drying.

Table 1

Quantitative and qualitative analysis of technical lignin

Index	Unit of measurement	Value
Moisture content (w^a)	wt. %	2.63
Ash content (A^d)	wt. %	27.45
Volatile matter yield (V^d)	wt. %	49.74
Total sulfur content (S_t^d)	wt. %	0.71
Carbon content (C^d)	wt. %	42.36
Hydrogen content (H^d)	wt. %	4.26
Nitrogen content (N^d)	wt. %	0.61
Oxygen content (O_d^d)	wt. %	24.61

The binder material used was BND 70/100 bitumen produced by PJSC “Ukratnafta” (Kremenchuk, Ukraine). The combination of bitumen with lignin was performed for 2 hours at a temperature of 180 °C with a stirring speed of 800 rpm. Subsequently, the main indicators, including penetration at 25 °C, softening point, adhesion to gravel, ductility at 25 °C, elastic recovery at 25 °C, and resistance to hardening at 163 °C (RTFOT method), were determined according to standardized test methods.

Results and Discussion

The test results of the obtained lignin-modified bitumen samples are shown in Table 2. For comparison, Table 2 also shows the characteristics of the initial bitumen mixed under the same conditions without lignin.

Table 2

The physicommechanical characteristics of the binder

Index	BND 70/100		BND 70/100 + technical lignin, wt. %			
	The initial (sample 1)	After mixing (sample 2)	1.0 % (sample 3)	3.0 % (sample 4)	5.0 % (sample 5)	7.0 % (sample 6)
Penetration at 25 °C, dmm	78	41	42	35	33	28
Softening point, °C	52.8	60.6	61.1	65.6	66.4	67.4
Adhesion to gravel, mark	4.0	4.0	4.0	4.0	4.0	4.0
Ductility at 25 °C, cm	58	25.5	24.0	17.5	15.5	12.0
Elastic recovery at 25 °C, %	17.5	17.0	24.0	22.0	21.0	21.5
Resistance to hardening at 163 °C:						
mass change, wt. %	0.086	0.10	0.154	0.215	0.273	0.28
softening point after RTFOT, °C	59.6	67.2	68.8	73.6	74.8	76.2
penetration at 25 °C after RTFOT, dmm	39	31	28	25	23	22
softening point change, °C	6.8	6.6	7.7	8.0	8.4	8.8
retained penetration, %	50.0	75.6	66.6	71.4	69.7	78.6

Based on the results presented in Table 2, it is evident that the binder rapidly loses its performance characteristics during the combination of bitumen with unpurified lignin. This is particularly observed through a decrease in penetration value from 78 to 28 dmm, an increase in the softening point by 15.6 °C, and a reduction in ductility from 58 to 12 cm. At the same time, the adhesion of bitumen does not deteriorate. However, this is likely due to the increase in its viscosity as a result of prolonged exposure to sufficiently high temperatures rather than the influence of lignin.

Considering the results obtained after aging of the bitumen-lignin mixture, it can also be stated that the influence of lignin on the binder is practically absent, and in some cases, even worsens the bitumen properties. This is particularly evident in the change of the softening point after RTFOT, which increases by 8.8 °C compared to the original sample (6.8 °C) and the mixed sample (6.6 °C). This can be explained by the negative impact of the high mixing temperature (180 °C), which is critical for bitumen properties. Regarding other indicators obtained after aging by the RTFOT method, the residual penetration and mass change values for sample 2 (without lignin) and samples 3-6 are practically identical.

Conclusions

Assessing the impact of technical lignin on the properties of road petroleum bitumen allows concluding that the use of technical lignin as a bitumen modifier to improve its operational properties is impractical.

On the other hand, it is evident that bitumen containing 1.0 wt.% lignin (sample 3) demonstrates characteristics nearly identical to sample 2 (the original bitumen mixed under the same conditions but without lignin). Therefore, it can be argued that in small quantities (in this case, 1.0 wt.%), lignin can serve as a relatively inexpensive substitute for significantly more expensive road petroleum bitumen.

It is also worth noting that technical lignin does not fully dissolve in bitumen. All mixtures obtained using technical lignin (samples 3-6) were heterogeneous. This is a significant drawback, as global and national regulatory documents related to bitumen modified with various additives require complete dissolution of modifiers in the binder. However, it should be considered that during the preparation of asphalt concrete mixtures for road construction or repair, various fillers, such as mineral powders, are added, which are also insoluble in bitumen. Therefore, it can be assumed that the insolubility of technical lignin in bitumen will not affect the final goal – obtaining high-quality asphalt concrete.

Based on the obtained results, the objectives of the next stages of the work were also determined, in particular:

- increasing the lignin content in bitumen without deteriorating its characteristics;
- selecting such conditions for combining lignin with bitumen that would minimize the negative impact of the mixing process on the binder's properties, which is likely achievable primarily by reducing the mixing temperature.

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Synthesis and Properties of Latex Composites Filled with PVA Hydrogel and Keratin

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Abstract. *This study explores the synthesis and characterization of latex composites with poly(vinyl alcohol) (PVA) hydrogel and keratin. The focus is on assessing mechanical strength, thermal stability, water absorption, and biodegradability, highlighting their potential for applications in agriculture, packaging, and biomedical engineering.*

Keywords: latex composites, PVA hydrogel, keratin, biodegradable materials, mechanical properties, thermal stability, water absorption

Introduction

The increasing environmental concerns and the imperative for sustainable development have intensified research into biodegradable materials. Natural rubber latex, known for its elasticity, film-forming capabilities, and biocompatibility, serves as a versatile matrix in composite materials. Enhancing its properties through the incorporation of biodegradable fillers has garnered significant attention, as it allows the development of materials with tailored mechanical, thermal, and environmental properties suitable for various applications.

Poly(vinyl alcohol) (PVA) is a synthetic polymer recognized for its excellent film-forming, emulsifying, and adhesive properties. Its hydrophilic nature and biodegradability make it an ideal candidate for environmentally friendly materials. PVA hydrogels have been widely studied due to their remarkable water retention capacity, mechanical strength, and biocompatibility, making them suitable for biomedical applications such as wound dressings, drug delivery systems, and tissue engineering scaffolds [1]. Moreover, PVA-based hydrogels have been explored for their ability to form strong intermolecular interactions with various natural polymers, further enhancing their properties [2].

Keratin, a fibrous structural protein commonly found in animal sources such as wool, feathers, and hair, has been extensively studied for its potential in the development of biocomposites due to its excellent biocompatibility, biodegradability, and mechanical reinforcement capabilities. Keratin-based materials exhibit remarkable structural properties owing to the presence of disulfide bonds and hydrogen bonding within their molecular structure [3]. Studies have shown that keratin can be effectively combined with both natural and synthetic polymers to improve the mechanical, thermal, and barrier properties of composite materials [4].

Recent studies have emphasized the creation of keratin-based biocomposites, reinforced and cross-linked with dual-functional cellulose nanocrystals, to significantly enhance their mechanical strength, structural integrity, and long-term stability in various environmental conditions [5]. Additionally, keratin's ability to form hydrogen bonds with hydrophilic polymers like PVA has been highlighted in literature as a promising strategy to develop materials with enhanced mechanical properties and biodegradability [6].

The integration of PVA and keratin in latex matrices has the potential to produce materials with unique properties, such as increased tensile strength, improved thermal stability, and controlled biodegradability. These materials are of significant interest in various industries, including agriculture, where biodegradable films are used for mulching and soil stabilization, in packaging as eco-friendly alternatives to traditional plastics, and in biomedical engineering for

biodegradable implants and drug delivery systems. Furthermore, the combination of PVA's hydrophilic nature and keratin's structural properties could lead to composites with superior moisture management and barrier functionalities, expanding their application range [7].

This study aims to synthesize and characterize latex composites filled with PVA hydrogel and keratin, evaluating their mechanical, thermal, and chemical properties. By varying the proportions of PVA and keratin, we seek to determine the optimal composition that balances strength, flexibility, and biodegradability. The comprehensive characterization of these materials provides valuable insights into their potential for diverse applications, contributing to the advancement of sustainable materials for agriculture, packaging, and biomedical engineering.

Materials and Methods

The composites were synthesized by incorporating PVA hydrogel and keratin into a latex matrix. A pure latex film without any additives was used as a reference sample (REF) to evaluate the effect of modifications. Samples S1, S2, and S3 represent composites with varying ratios of PVA hydrogel and keratin, where S1 contains the highest keratin content, S3 the lowest, and S2 represents an intermediate composition. These variations allowed for the assessment of the influence of keratin and PVA content on the composites' mechanical, thermal, and moisture properties. The keratin, sourced from bovine hair and bird feathers, was milled and sieved to ensure uniform particle size distribution.

The PVA hydrogel was prepared by dissolving PVA powder in deionized water at elevated temperatures under constant stirring until a clear solution was obtained, followed by cooling to room temperature to form the hydrogel. The latex films were prepared by blending the components to ensure homogeneity, followed by casting onto Petri dishes and drying at 40°C for 24 hours.

To evaluate the physical, chemical, and thermal properties of the composites, a series of tests was conducted to ensure comprehensive characterization.

Mechanical properties, including tensile strength and elongation at break, were measured using a universal testing machine (Instron 3345) with a 500 N load cell at a crosshead speed of 10 mm/min, following ASTM D412 standards. Shore A hardness was determined using a durometer (Shore Instruments) in accordance with ASTM D2240.

Chemical interactions between latex, PVA hydrogel, and keratin were analyzed using Fourier-transform infrared spectroscopy (FTIR) with a Nicolet iS10 spectrometer in the range of 4000–400 cm^{-1} . This helped identify functional groups such as hydroxyl (O-H), carbonyl (C=O), and amide bonds.

Surface morphology was examined with scanning electron microscopy (SEM, JEOL JSM-6390) at 15 kV, providing insights into the dispersion of keratin particles within the latex matrix.

Thermal stability was evaluated using thermogravimetric analysis (TGA) on a TA Instruments Q500. Samples were heated from 25°C to 600°C at 10°C/min under a nitrogen atmosphere, recording degradation temperatures and residual weight.

Moisture properties were assessed by immersing samples in distilled water at 25°C for 24 hours, following ASTM D570 standards. Water absorption percentage was calculated based on weight differences before and after immersion.

This evaluation provided a thorough understanding of the composites' performance, supporting their optimization for various applications.

Results and Discussion

Mechanical testing revealed that the addition of PVA hydrogel significantly improved the flexibility and water retention properties of the composites. This enhancement can be attributed to the hydrophilic nature of PVA, which allows the composite matrix to retain more moisture, thus

increasing its elasticity. In contrast, the REF sample, composed solely of latex, exhibited lower flexibility and no water retention capabilities, underscoring the critical role of PVA in enhancing these properties.

The incorporation of keratin contributed to a notable increase in tensile strength and hardness due to its structural reinforcement capabilities. Sample S1, with the highest keratin content, exhibited the most robust mechanical performance, achieving a tensile strength of 2.69 MPa (Table 1). This suggests that keratin's fibrous structure effectively reinforces the latex matrix, providing resistance to deformation under stress. Conversely, sample S3, with the lowest keratin content and highest PVA concentration, demonstrated increased flexibility but reduced tensile strength (1.53 MPa), indicating the inherent trade-off between rigidity and elasticity in composite design.

Shore A hardness values also reflected the reinforcing effect of keratin. Sample S1 displayed the highest hardness at 63, while S3 exhibited a lower hardness of 57. This trend confirms that higher keratin content enhances the composite's structural integrity, providing greater resistance to surface deformation under applied force.

Table 1

Mechanical Properties of Latex Composites and Reference Sample

Sample ID	Tensile Strength (MPa)	Shore A Hardness
S1	2.69 ± 0.05	63 ± 2
S2	2.36 ± 0.06	60 ± 2
S3	1.53 ± 0.07	57 ± 3
REF	1.10 ± 0.04	50 ± 2

The FTIR spectra confirmed the presence of characteristic functional groups from both PVA and keratin, indicating successful integration within the latex matrix. Prominent peaks corresponding to hydroxyl groups from PVA (3200–3400 cm⁻¹) and amide groups from keratin (1650 cm⁻¹ for amide I and 1540 cm⁻¹ for amide II) were observed. These interactions suggest the formation of hydrogen bonds between PVA and keratin, contributing to the enhanced mechanical stability and cohesive strength of the composites.

SEM images provided further insights into the microstructural properties of the composites. Keratin particles were well-dispersed within the latex matrix, forming a uniform and continuous composite structure. The addition of PVA hydrogel resulted in a smoother surface morphology, beneficial for applications requiring barrier properties, such as packaging materials. In contrast, the REF sample displayed a relatively rougher surface, lacking the homogeneous texture observed in the modified composites, which may limit its performance in moisture-sensitive environments.

Thermogravimetric analysis (TGA) indicated that the composites exhibited improved thermal stability compared to pure latex films. The onset degradation temperature increased by approximately 15°C in sample S1, highlighting the thermal stabilizing effect of keratin. This enhancement is likely due to keratin's robust molecular structure, which provides resistance to thermal degradation, thereby extending the material's thermal tolerance range.

Table 2

Thermal and Moisture Properties of Latex Composites and Reference Sample

Sample ID	Onset Degradation Temperature (°C)	Water Absorption (%)
S1	245 ± 3	18 ± 0.9
S2	240 ± 4	22 ± 1.0
S3	235 ± 5	27 ± 1.2
REF	220 ± 2	0 (hydrophobic)

Water absorption tests showed that sample S3, with the highest PVA content, had the greatest water retention capacity (27%), making it highly suitable for applications in moisture-sensitive environments. In contrast, the REF sample did not exhibit any water absorption, confirming the hydrophobic nature of pure latex and the significant hydrophilic effect introduced by PVA.

In comparison to the REF sample (pure latex film), the composites demonstrated significant improvements in tensile strength, hardness, thermal stability, and water retention. These results confirm the effectiveness of PVA and keratin as multifunctional reinforcing agents in enhancing the performance of latex composites. The study suggests that optimizing the ratio of PVA to keratin can tailor the mechanical, thermal, and moisture properties of these composites, making them suitable for diverse applications, including biodegradable packaging, agricultural films, and biomedical materials.

Conclusions

The results of this study clearly demonstrate the potential of combining latex, PVA hydrogel, and keratin to create biodegradable composites with tailored mechanical and thermal properties. The synergistic effect of PVA's hydrophilicity and keratin's structural reinforcement resulted in composites with enhanced tensile strength, improved thermal stability, and superior water absorption capabilities. These materials exhibited significant improvements over pure latex films, highlighting their suitability for applications in agriculture, packaging, and biodegradable films where mechanical durability, thermal stability, and environmental compatibility are essential. In agricultural applications, such composites could serve as biodegradable mulching films, offering both mechanical protection and moisture retention while decomposing naturally after use.

Further studies will also evaluate the barrier properties of these composites against gases and moisture, which are critical for packaging applications. The development of these latex-based composites with PVA hydrogel and keratin not only contributes to the advancement of sustainable materials but also opens new avenues for environmentally friendly solutions across multiple industries. The continued optimization of these materials will be pivotal in addressing global sustainability challenges.

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Formation of Specific Electrical Resistance of Blast Furnace Coke Under the Influence of Raw Materials and Technological Factors of Its Production

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Abstract. *The studies made it possible to establish the relationship between the specific electrical resistance and the reactivity, To obtain high-strength coke with low abrasiveness, it is necessary to have an appropriate component composition of the coal charge with a sufficient level of sintering, an optimal level of its grinding and an appropriate thermal regime of its coking.*

Keywords: electrical resistance, coke powder, coal mixture, grade composition, structural strength, optimization.

Introduction

The quality of coke is a key factor for satisfactory operation of the furnace and can be evaluated in terms of physical characteristics (abrasion and crushing resistance, particle size distribution), chemical composition, coke reactivity index, and post-reaction strength of the coke. The most important characteristics of coke used in electrothermal production are reactivity, electrical conductivity (specific electrical resistance), thermal stability, and technical analysis indicators (ash content, volatile matter yield). In electrothermal processes, coke acts as a reducing agent. Raw materials and coking process factors determine the carbon structure of blast furnace coke and its physical and mechanical properties. Deeper thermochemical transformations of coal matter also lead to an improvement in the coke structure.

I Determination of electrical resistivity

The degree of orderliness of the structure of coke and other carbonaceous materials can be controlled by the resistivity. Given that the resistivity is considered an indicator of the structural features of carbon materials, its value will be determined by both raw material factors and the impact of coking technology.

The aim of the work was to theoretically and experimentally substantiate the relationship between the resistivity and the orderliness of its structure [1]. A comprehensive assessment of the properties of the experimental cokes as lumpy material (П25, П10), porous coke body devoid of cracks (structural strength by Gryaznov, reactivity CRI and km, apparent density, porosity); as well as the substance of coke that forms the pore walls (abrasive hardness by Ginzburg and actual density) was given.

Coal charges of different component compositions were used for the study.

The resistivity of coke was determined in accordance with DSTU 8831:2019 “Coke. Method for determination of the resistivity of coal coke powder”, which establishes a method for measuring the resistivity of coal coke powder in the range from 0.05 Ohm-cm to 0.5 Ohm-cm. The installation for measuring the resistivity of coke powder, according to DSTU 8831:2019, is shown in Fig. 1.

It has been established that an increase in the content of gas group coal is the dominant factor affecting the properties of coke, hence increasing the reactivity of coke and naturally increasing the resistivity of the resulting coke.

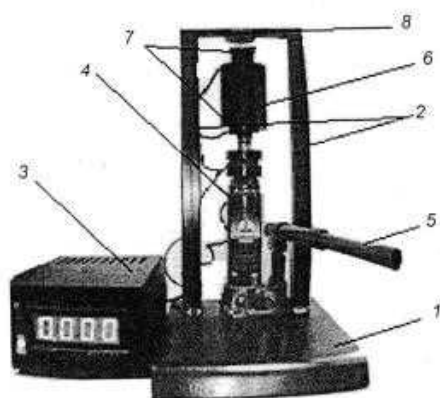


Fig. 1. Test setup for determining the electrical resistance of coke powder:
1 - frame; 2 - racks; 3 - digital measuring unit with a current stabilizer and a digital millivoltmeter; 4 - hydraulic jack, 2 kN; 5 - jack handle; 6 - two-probe measuring matrix; 7 - upper and lower punches; 8 - crossbar.

The essence of this method is to measure the voltage drop when a direct current passes through a compressed column of coke with a particle size of less than 0.2 mm, enclosed in a matrix between two punches.

A scheme of the laboratory setup for experimental coking is shown in Fig. 2

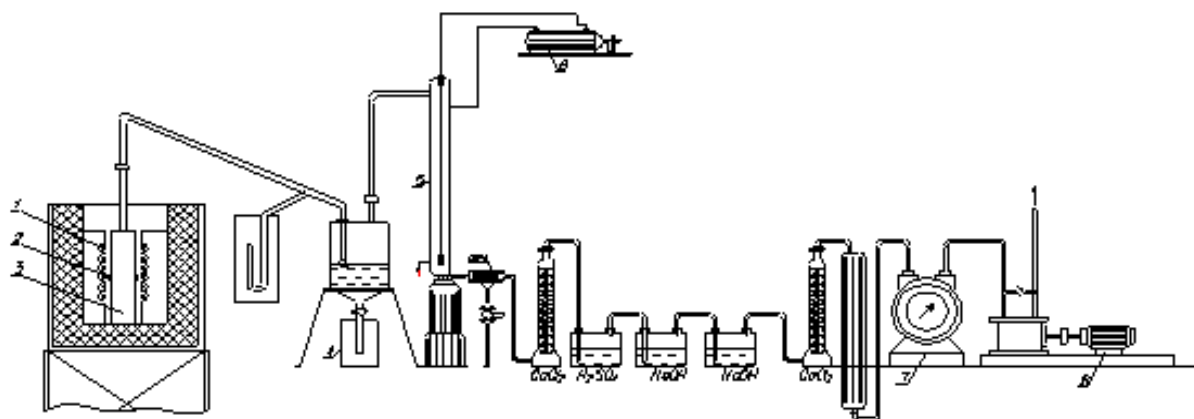


Fig. 2. Scheme of the laboratory setup: 1 - carborundum heater; 2 - thermocouple covers; 3 - chamber; 4 - resin collector; 5 - electrostatic precipitator; 6 - transformer; 7 - gas meter; 8 - pump.

It has been found that the structure of blast furnace coke is significantly affected by the grade composition of the coal charge, sinterability, and coking properties of its components, which can be further evaluated using the resistivity.

According to the results of the study, the relationship between the resistivity of coke and the chemical properties of coke (reactivity and post-reaction strength) was established.

It was found that a change in the grade composition of the coal charge due to an increase in the content of low-metamorphosed coal (42-63 %), as a result, causes a decrease in the vitrinite reflection index and a shift in the plasticity interval towards lower temperatures, and also leads to a weakening of the coke structure and an increase in its resistivity [2].

Specific electrical resistance is an aggregate characteristic of coke properties, as evidenced by the mathematical dependence of the change in resistivity on ash content, sulfur content, volatile yield, and petrographic composition, and high correlation values (0,6-0,84).

The studies made it possible to establish the relationship between the resistivity and reactivity, which is reasonable, since both of these indicators characterize the structure of coke and the degree of its orderliness. The obtained regression equations will allow us to further assess the structure of coke and predict its behavior in the blast furnace process. They can also be recommended for optimizing the component composition and quality of production batches, given their significant impact on the resistivity of coke. This is especially relevant when using coke in electrothermal processes, since the resistivity of coke determines the productivity, electrical and thermal efficiency factor of the furnace.

II Influence of organic and inorganic additives on the specific electrical resistance of coke

The effect of organic (petroleum coke) and inorganic (boron carbide and silicon carbide (carborundum) nanopowders) additives on the quality of coke produced in a laboratory furnace and its electrical properties was evaluated.

The coal concentrates were studied by the following methods of express analysis (W^r , A^d , S^d , V^{daf}), plastometric (X , Y), and petrographic (R_0 , petrographic composition).

After coking, the gross coke yield and technical analysis parameters were determined (A^d , S^d , V^{daf}), mechanical strength (M_{25} , M_{10}), structural strength (CM), abrasive hardness (AT), and specific electrical resistance of coke (ρ).

Coal charge with organic additive. Four variants of coal mixtures that are typical for coal blends of Ukrainian coke plants were studied. Analyzing the results of determining the quality of the coke produced, it can be stated that the addition of 5% of petroleum coke to coal blends leads to an increase in the gross coke yield by 1.2-1.3%; a decrease in coke ash content by 0.2-0.3%; increase in total sulfur content in coke by 0.15-0.23%; deterioration of both mechanical (II25 - by 0.1-0.6%; II10 - by 0.1-0.2%) and post-reaction (CSR - by 0.6-1.0%) strength, coke reactivity (CRI - by 0.2-0.3%), as well as structural strength (SS - by 0.3-0.4%), abrasive hardness (AT - by 0.7-1.0 mg) and specific electrical resistance (ρ - by 0.002-0.007 Ohm $\times$ cm).

Petroleum coke, as an inert material, significantly worsens the flowability of coal, but some interaction with coal can occur due to the release of volatile substances from petroleum coke, which smooths out this negative effect [3]. In addition, there was no significant effect of petroleum coke on the type of coke texture. All coke matrices (binder phase) were formed by ring texture components, the proportion of which decreased with increasing participation of petroleum coke.

Coal charge with inorganic additive. The additives were introduced into the production charge from the coal preparation shop of «PrAT Zaporozhkoks». The additives are crystalline nanopowders of boron carbide and silicon carbide (carborundum) produced by the Research Institute of Refractories, Fig. 3.

It has been shown that the introduction of a certain amount (0.25 wt. %) of non-sintering B₄C and SiC nanoparticles allows modifying the processes occurring during the plasticization of coal charge, with a subsequent increase in coke strength. The effect on coke properties of B₄C and SiC nanoparticles depends significantly on the rank composition of the charge. The proposed additives are especially effective in the charge with low coking properties.

The effect of adding inorganic nanoadditives to the charge is illustrated in Fig. 4

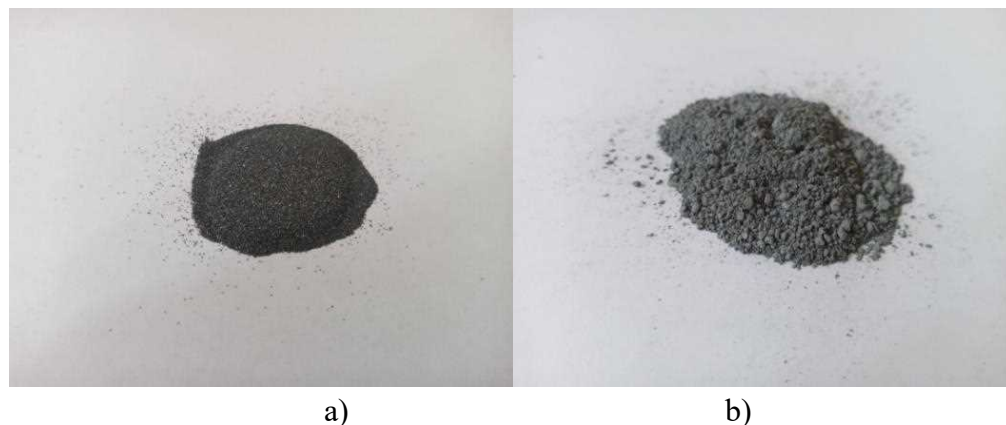


Fig. 3 Nanopowder: a) boron carbide; b) silicon carbide.

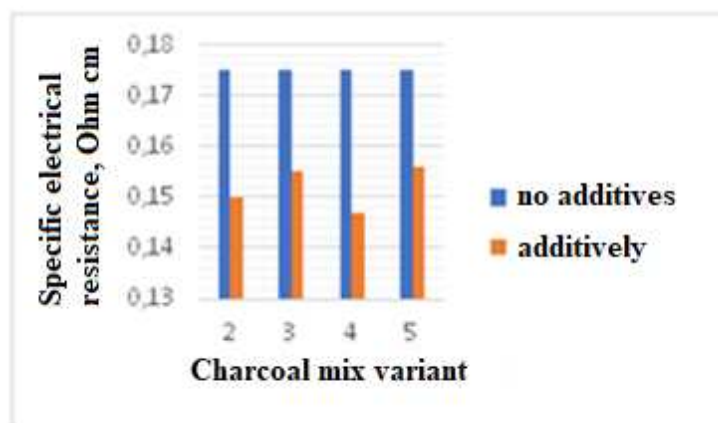


Fig. 4. Resistivity depending on the coal mixture variant

Conclusions

The structure of blast furnace coke is significantly influenced by the grade composition of the coal charge, sinterability, and coking properties of its components, which can be further evaluated using specific electrical resistance.

Increasing the degree of coke readiness and increasing the degree of orderliness of its structure leads to a decrease in the coke-specific electrical resistance.

The specific electrical resistance is a measure of the temperature effect during the thermal destruction of coal and the coking process. Depending on the final temperature of the process, the resistivity decreases as the temperature increases. Therefore, the specific electrical resistance can characterize the degree of coke readiness.

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Intensification of Evaporation of Sulfuric Acid Solutions

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Abstract. *The conditions of evaporation of a sulfuric acid drop moving in a gas stream are considered. The influence of intensifying factors (initial temperature and drop velocity) on the evaporation of a single drop is investigated. It is shown that the evaporation of sulfuric acid solutions in a hollow column apparatus is inefficient. It is theoretically substantiated that multiple dispersion of the liquid and high values of the relative droplet velocity significantly reduce the evaporation time.*

Keywords: evaporation, hydrolytic sulfuric acid, exhaust gases, mathematical modeling.

Introduction

Sulfuric acid (H_2SO_4) is an important chemical widely used in various industrial processes. However, its use leads to the generation of significant amounts of waste acid, which requires efficient methods of recycling and disposal. Proper management of this waste is key to reducing negative environmental impacts and promoting resource recovery.

The sulphate method of producing pigment titanium dioxide (TiO_2) involves significant amounts of hydrolytic sulphuric acid (HSA). The production of 1 ton of TiO_2 generates approximately 5...6 tons of HSA with a concentration of 18...25% H_2SO_4 and 5...6.5% FeSO_4 [1]. This waste is often not recycled but dumped into tailings, which leads to environmental problems and loss of valuable acid. Global production of pigment TiO_2 exceeds 8 million tons per year [2] and is showing an upward trend. More than half of these volumes are produced by the sulphate method, and in Ukraine, all TiO_2 is produced by this method, which leads to the accumulation of large volumes of HSA. The accumulation of hydrolytic sulfuric acid is a serious environmental problem. The lack of proper disposal of this waste can lead to soil and water pollution, which negatively affects ecosystems and public health. Therefore, the development and implementation of effective methods of HSA utilization is an urgent task for the industry.

Modern approaches to the utilization of waste sulfuric acid include [3, 4]:

- Acid regeneration: This approach involves the purification and reuse of sulfuric acid in the process, which reduces waste and the cost of purchasing new acid.
- Production of by-products: Waste acid can be used to produce other chemicals, such as ammonium sulfate or iron oxide pigments, which helps to reduce the environmental burden and generate additional economic benefits.
- Neutralization and safe storage: In cases where recovery or recycling is not possible, the waste acid is neutralized with alkalis to form salts, which are then safely stored or used in other industries.

Previous studies have theoretically [5-7] and practically confirmed [1] the feasibility of utilizing hydrofluoric acid solutions by evaporating them in direct contact with hot exhaust gases generated during the production of pigmented titanium(IV) dioxide. This method significantly

reduces the cost of evaporation and recovers the heat of the exhaust gases. This approach produces sulfuric acid with a concentration of 55...70%, which meets the requirements for the production of mineral fertilizers (concentration $\text{H}_2\text{SO}_4 \geq 55\%$, Fe content $\leq 0.5\%$).

To analyze this process, we used a mathematical model [5] that describes the heat and mass transfer between sulfuric acid droplets and a hot gas stream. This model makes it possible to determine the main parameters of the process, in particular, the evaporation rate of droplets and changes in their size while moving in the gas medium. This, in turn, helps to optimize the technological parameters of the evaporation process, which increases production efficiency and reduces energy costs.

In particular, studies have shown that the evaporation rate of sulfuric acid droplets depends on the acid concentration, temperature, and gas flow rate. At the same time, the developed mathematical models allow predicting the behavior of droplets under different conditions, which is useful for improving technological processes in the chemical industry. In view of this, **the purpose of this work** is to theoretically study methods for intensifying the evaporation of dilute sulfuric acid solutions.

To achieve this goal, it was necessary to solve the following tasks: to theoretically analyze the influence of physical factors on the evaporation rate; to establish a technologically feasible evaporation regime.

Methods of calculation

To determine the evaporation rate, we used the developed model "sulfuric acid droplet - heated gas" [5]. In previous studies [6], mathematical dependences were derived for the heating time (τ_0') and evaporation time (τ_0'') of a drop moving countercurrently in a hot air flow under the action of gravity (equations 1, 2). Initial conditions: the velocity and temperature of the droplet are $v_{20} = 0$ m/s and $T_2 = 293$ K, respectively; the air velocity, temperature, and moisture content remain constant and are $v_1 = 1$ m/s; $T_1 = 373...773$ K and $x = 10.5 \cdot 10^{-3}$ kg/kg, respectively.

$$\tau_0' = 1.36 \cdot 10^4 \cdot d_{20}^{1.38} / \exp(0.0025 \cdot \Delta T_{1-2}), \quad (1)$$

$$\tau_0'' = 9 \cdot 10^5 \cdot \Delta C^{0.7} \cdot d_{20}^{1.35} / \Delta T_{1-2}, \quad (2)$$

$$\tau_0 = \tau_0' + \tau_0'' \quad (3)$$

where ΔT_{1-2} - is the average driving force of the heating and evaporation processes, K; ΔC is the increase in the concentration of H_2SO_4 , ($\Delta C = C_{2(N)} - C_{20}$), C_{20} , $C_{2(N)}$ are the initial and final concentrations of H_2SO_4 , respectively, %.

The temperatures of the drop at the beginning (T_2') and at the end of the evaporation stage (T_2'') actually correspond to the wet thermometer temperatures for acid solutions with an initial concentration of C_{20} and a final concentration of $C_{2(N)}$. In [7], for acid solutions with a concentration of $C_{20} = 20$ and $C_{2(N)} = 70\%$ and the above conditions, the following dependencies were derived:

$$T_2' = 12.8 \cdot \ln(\Delta T) + 248.6, \quad (4)$$

$$T_2'' = 20.5 \cdot \ln(\Delta T) + 260.3. \quad (5)$$

The calculation of the droplet velocity and its displacement was performed using the numerical Euler method. To ensure the accuracy of the calculations, the time interval ($\Delta \tau$) was chosen to be 0.005 s. The calculations were repeated N times until the required acid concentration was reached (maximum 70% H_2SO_4). The time of contact of the droplet with the air flow was determined as

$$\tau = N \cdot \Delta\tau. \quad (6)$$

The effect of intensifying factors was expressed as a relative decrease in contact time (δ , %) compared to τ_0 , which was calculated for a droplet using Equations 1...3. The calculation of the relative decrease in contact time was determined by the formula

$$\delta = |\tau_0 - \tau| \cdot 100 / \tau_0. \quad (7)$$

Research results and discussion

Provided that the gas parameters are stable, the factors that influence the sulfuric acid droplet-heated gas system are the temperature, diameter, and velocity of the droplet.

The contact time consists of the heating and evaporation time (3), so a preheated droplet will evaporate more rapidly. It is economically and technologically feasible to preheat the solution to the wet bulb temperature T_2'' of the evaporating droplet. As the droplet velocity increases, the relative velocity of the phases and, accordingly, the heat and mass transfer coefficients increase, and thus the evaporation time decreases.

To determine the intensifying effect of these factors, using the mathematical model [5], we calculated the contact time and its relative decrease at initial temperatures $T_{20}=T_2''$ (Table 1) and in the range of initial droplet velocities $v_{20}=5...20$ m/s (Table 2).

Table 1

Influence of the initial droplet temperature ($T_{20} = T_2''$, K) on the contact time (τ , s) and its relative decrease (δ , %)

Temperature, K		Initial droplet diameter $d_{20} \cdot 10^3$, m							
		0.5		1		1.5		2	
T_1	T_2''	τ , s	δ , %	τ , s	δ , %	τ , s	δ , %	τ , s	δ , %
373	349.3	11.0	7.1	27.9	6.9	47.5	6.9	69.1	6.9
473	367.3	3.7	10.7	9.6	10.5	16.3	10.4	23.8	10.4
573	376.3	2.1	12.7	5.4	12.2	9.3	12.1	13.5	12.1
673	381.9	1.4	13.8	3.7	13.3	6.3	13.2	9.2	13.1
773	385.7	1.0	14.6	2.8	13.9	4.8	13.8	6.9	13.8

($C_{20} = 20\%$; $C_{2(N)} = 70\%$; $v_{20} = 0$ m/s; $v_1 = 1$ m/s)

Table 2

Effect of the initial droplet velocity ($v_{(20)}$, m/s) on the contact time (τ , s) and its relative decrease (δ , %)

v_{20} , m/s	Initial droplet diameter $d_{20} \cdot 10^3$, m							
	0.5		1		1.5		2	
	τ , s	δ , %	τ , s	δ , %	τ , s	δ , %	τ , s	δ , %
$T_1 = 373$ K								
5	11.7	0.8	29.8	0.5	50.8	0.3	74.0	0.3
10	11.7	1.2	29.8	0.7	50.8	0.5	73.9	0.4
20	11.6	1.5	29.7	1.0	50.7	0.7	73.7	0.6
$T_1 = 573$ K								
5	2.3	3.6	6.0	2.4	10.4	1.7	15.2	1.3
10	2.2	5.5	5.9	3.6	10.3	2.6	15.1	2.0
20	2.2	7.6	5.8	5.2	10.2	3.7	14.9	3.0
$T_1 = 773$ K								
5	1.1	6.7	3.1	4.4	5.3	3.2	7.8	2.5
10	1.1	10.0	3.0	6.9	5.2	5.1	7.7	4.0
20	1.0	14.2	2.9	9.8	5.1	7.3	7.6	6.0

($T_{20} = 293$ K; $C_{20} = 20\%$; $C_{2(N)} = 70\%$; $T_{20} = 293$ K, $v_1 = 1$ m/s)

The calculation results show that preheating the droplet to a temperature of T_2'' slightly reduces the contact time (6.9...14.6 %), and the relative decrease in the evaporation duration depends little on its diameter, but is mostly determined by the initial temperature (Table 1). An increase in the initial droplet velocity has a more significant effect on the evaporation rate of small droplets, but the relative decrease in the evaporation duration does not exceed 14.2 % (Table 2).

This is due to the fact that the intensifying effect of droplet temperature and velocity is short-lived and has a noticeable effect at the initial moment of contact with air, i.e., at the stage of droplet heating and initial acceleration. During the main time of evaporation, the temperature and velocity of the droplet are equalized, and the process characteristics are practically independent of the initial droplet parameters.

Better evaporation rates can be achieved by simultaneously increasing the initial temperature and droplet velocity (Table 3).

The calculation results show that preheating the droplet to a temperature of T_2'' reduces the contact time by 6.9-14.6%, and the relative reduction in the evaporation duration depends little on its diameter, but is mostly determined by the initial temperature (Table 1). An increase in the initial droplet velocity has a more significant effect on the evaporation rate of small droplets, but the relative reduction in the evaporation time does not exceed 14.2% (Table 2). This is explained by the fact that the intensifying effect of the temperature and droplet velocity is short-lived and manifests itself mainly at the initial stage of contact of the droplet with air, i.e., during its heating and initial acceleration. During the main period of evaporation, the temperature and velocity of the droplet equalize, and the process characteristics are practically independent of the initial droplet parameters. The best evaporation rates can be achieved by simultaneously increasing the initial temperature and droplet velocity (Table 3).

Table 3

Influence of initial temperature ($T_{20} = T_2''$, K) and droplet velocity (v_{20} , m/s) on contact time (τ , s) and its relative decrease (δ %)

v_{20} , m/s	Initial droplet diameter $d_{20} \cdot 10^3$, m							
	0.5		1		1.5		2	
	τ , s	δ , %	τ , s	δ , %	τ , s	δ , %	τ , s	δ , %
$T_1=373$ K; $T_2''= 349.3$K								
5	10.8	8.3	27.7	7.5	47.3	7.3	68.9	7.1
10	10.8	8.8	27.6	7.8	47.2	7.5	68.8	7.3
20	10.7	9.3	27.5	8.1	47.1	7.8	68.7	7.4
$T_1=573$ K; $T_2''= 376.3$K								
5	1.9	18.5	5.3	14.6	9.1	14.1	13.3	13.4
10	1.9	20.7	5.2	15.8	9.0	15.1	13.2	14.1
20	1.8	23.5	5.1	17.3	8.8	16.4	13.1	15.1
$T_1=773$ K; $T_2''= 385.7$K								
5	0.9	25.5	2.6	19.5	4.5	17.6	6.7	16.3
10	0.8	29.7	2.5	22.3	4.4	19.6	6.6	17.8
20	0.8	35.1	2.4	25.6	4.3	22.1	6.5	19.7

($C_{20} = 20\%$; $C_{2(N)} = 70\%$; $v_1 = 1$ m/s)

The intensity of the evaporator depends not only on the contact time but also on its geometric dimensions. For column-type hollow atomizers, the determining parameter is their height. The best

technical and economic performance is achieved by column-type devices, in which the acid concentration reaches the specified final value in one drop pass. Therefore, the distance r_2 that the droplet travels during contact determines the height of the evaporator column. The calculation results are shown in Table 4.

Table 4

Distance (r_2 , m) traveled by a drop during contact time (τ , s)

v_{20} , m/s	Initial droplet diameter $d_{20} \cdot 10^3$, m			
	0.5	1.0	1.5	2.0
$T_1 = 373K$				
0	11.28	82.57	210.31	389.43
5	10.48	75.90	193.30	358.44
10	10.84	76.54	194.13	359.60
20	11.31	77.44	195.38	361.32
$T_1 = 573K$				
0	2.18	18.72	50.01	94.79
5	2.29	16.78	43.63	82.43
10	2.72	17.64	44.76	83.89
20	3.34	18.91	46.45	86.18
$T_1 = 773K$				
0	0.97	9.74	27.39	53.29
5	1.31	8.93	23.86	45.88
10	1.77	9.87	25.17	47.57
20	2.46	11.33	27.25	50.31

($T_{20} = T_2''$; $C_{20} = 20\%$; $C_{2(N)} = 70\%$; $v_1 = 1$ m/s)

The calculations show that it is possible to realize the evaporation process in one pass only if the initial droplet diameter is $d_{20} \leq 0,5 \cdot 10^{-3}$ m. In the case of a larger droplet diameter, the required column height increases significantly. Fine dispersion requires considerable energy resources and requires the use of highly efficient and corrosion-resistant droplet collectors. Thus, the evaporation of solutions of H_2SO_4 in hollow columns turns out to be inefficient and practically devoid of prospects for intensification. In the search for ways to improve the efficiency of this process, it was concluded that the goal can be achieved only by changing the evaporation regime and introducing an apparatus that better meets the technological needs.

Conclusions

1. Rational management of sulphuric acid waste in titanium dioxide production is an important task for environmental protection and optimal use of resources. The introduction of modern utilization technologies will help minimize environmental risks and ensure the sustainable development of the chemical industry.

2. The use of hollow columns for the evaporation of dispersed sulfuric acid solutions is an energy-intensive and technically inefficient solution.

3. Intensification of evaporation is possible by ensuring multiple dispersion of the liquid and achieving a high relative velocity between the dispersed droplets. The implementation of this mode will significantly reduce the duration of the evaporation process and efficiently use the energy of low-enthalpy gas emissions.

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Mechanical Properties of Biodegradable Films Based on Polyvinyl Alcohol and Starch

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Abstract. *The paper presents the results of obtaining and studying the physical and mechanical properties of biodegradable film materials based on polyvinyl alcohol with the addition of corn starch, sodium tetraborate, and glycerin. It was found that an increase in the concentration of sodium tetraborate and the aging of the films at a temperature of 433 K increases the tensile strength of the film samples. The results of the study of the obtained materials allow us to predict the possibility of their use as environmentally friendly packaging.*

Keywords: packaging materials, films, polyvinyl alcohol, starch, borax, exploitation properties.

Introduction

Polymeric plastic materials are widely used as packaging for almost all types of products due to their high performance characteristics and affordability. The use of synthetic polymer products is constantly growing. This leads to an increase in waste, which is problematic for disposal. In the natural environment, plastic materials biodegrade within 40-100 years, creating a huge burden on the environment. The combination of synthetic and natural polymers is an important way to produce modern packaging materials that are biodegradable after use. Water-soluble and biodegradable polymers are becoming the basis for composite materials for many applications. Films based on the water-soluble synthetic polymer polyvinyl alcohol (PVA) have already found practical application due to their high barrier characteristics and chemical stability. The creation of nanocomposites based on PVA allows the obtaining of materials with improved characteristics [1]. The physical and mechanical properties and ability to print films based on polyvinyl alcohol make it possible to use them as environmentally friendly packaging [2]. The combination of polyvinyl alcohol with polysaccharides improves the characteristics of film materials required for packaging products and increases their biodegradability [3, 4].

Biodegradable polyvinyl alcohol is a relatively expensive raw material. To reduce the cost of packaging materials, starch is an interesting natural biopolymer, a renewable raw material of plant origin. The combination of PVA with starch can improve the mechanical properties of films, such as tensile strength and moisture resistance [3-5]. The addition of cellulose to the mixture of polyvinyl alcohol and starch gives the composites additional reinforcement and increased tensile strength [6]. To improve water resistance, composites based on polyvinyl alcohol are subjected to heat treatment, which results in a stronger spatial mesh structure of polyvinyl alcohol [3].

PVA-based films containing corn starch undergo better degradation by enzymes, as well as in soil and compost, compared to films without starch [5,7]. The introduction of cassava starch and corn starch into polyvinyl alcohol significantly increases the biodegradation rate of films [8, 9, 10]. Studies of the biodegradation of composite materials based on polyvinyl alcohol and starch have shown that under the action of microorganisms in vermicompost, a fairly rapid destruction of the biopolymer occurs. At a content of 30% starch in the biopolymer composition, noticeable changes in the surface structure of the samples occur on day 20 [3]. The biodegradation of films made of plasticized starch and synthetic polymer in vermicompost takes an average of 30 days [10].

The goal of our work is to create film materials based on polyvinyl alcohol with the addition of corn starch, sodium tetraborate, and glycerin. The study of the physical and mechanical properties of the obtained materials will allow us to predict the possibility of their use as environmentally friendly packaging.

Materials and methods

Polyvinyl alcohol was used as a polymer base. It is a water-soluble, chemically resistant, non-toxic synthetic polymer. PVA films are transparent, durable, able to provide basic barrier properties for packaging, and can decompose in natural conditions within a short time. Polyvinyl alcohol with an average polymer chain length is promising for the creation of biopolymers [11], Mat Suki. The polymer Polyviol 6 04/140 we studied is white in appearance, in the form of small granules. Dissolution in water was carried out under heating until a homogeneous solution was obtained. The addition of a natural polymer, corn water-soluble starch, can change the properties of film materials and improve biodegradability. The solution was heated with stirring to the gelling temperature.

Glycerin FS 42-2202-84 was added as a plasticizer at room temperature. Glycerin increases the elasticity of the films. A more even distribution of polymer chains gives the films tensile strength and durability, which are important performance characteristics of packaging materials.

The addition of sodium tetraborate ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10 \text{ H}_2\text{O}$) will give the films antibacterial properties. This will allow the use of film materials for packaging medical products and food, providing protection against microorganisms [12]. In solution, sodium tetraborate hydrolyzes to form boric acid, which provides crosslinking of polyvinyl alcohol chains. Therefore, the introduction of sodium tetraborate into the composite improves the chemical stability and mechanical properties of the material during operation.

The films were obtained by sputtering on a glass substrate. The resulting films have a homogeneous structure and uniform thickness. Upon completion of the structure formation processes and complete drying, the liquids are easily separated from the substrate.

The mechanical properties of the films were studied on a universal tensile testing machine (dynamometer), with a distance between the clamps of 50 mm according to [13]. Tensile and strength tests were performed to determine the elasticity of the films, as well as their ability to withstand mechanical stress, which is important for packaging materials.

Results and discussion

Our studies show that the optimal mass ratio of polyvinyl alcohol and corn starch is 5:1-5:2 with the addition of sodium tetraborate in the amount of 10%-20% (relative to the dry PVA residue). The introduction of glycerin into the polymer composition allows us to obtain soft and elastic films with good tensile strength. To study the properties, films were made whose composition in terms of anhydrous substances is given in Table 1. The thickness of the obtained films is in the range of 0.0551-0.0635 mm. The obtained film samples were heat-treated at a temperature of 393 K (№ sample 2, 5) and 423 K (№ sample 3, 6) for 30 minutes. Heating the films above 433 K leads to yellowing of the samples, since they contain corn starch.

The breaking force and tensile strength of 15 mm wide samples made from the obtained biodegradable film materials were measured on a universal tensile testing machine (dynamometer). The obtained results are shown in Table 1.

The research results show that an increase in the borax content of film materials increases the tensile strength and tensile stress. When the film samples are heated, better crosslinking of the polymer base occurs and, as a result, the tensile strength of the material improves (Fig. 1).

Table 1

№ sample	Sample composition, mass %				Film thickness, [mm]	Breaking strength (P), [H]	Tensile (Δl), [mm]	Elongation at break, %
	Polyviol 6 04/140	Corn starch	Glycerin	Na ₂ B ₄ O ₇ ·10 H ₂ O				
1	45	10	40	5	0.0635	15.24	95	190
2	45	10	40	5	0.0615	17.15	90	180
3-	45	10	40	5	0.0551	13.23	69	138
4	40	10	40	10	0.0736	27.56	135	270
5	40	10	40	10	0.0658	17.27	110	220
6	40	10	40	10	0.0613	28.028	100	200

Since the tensile stress is the tensile load per unit area of the film cross-section at the moment of rupture, this value best characterizes the strength of film materials. The tensile strength σ (N/mm² або MPa) is calculated using the formula $\sigma = \frac{P}{S}$. Fig. 1 shows the change in tensile stress of films with a thickness of 0.0551 - 0.0615 mm as a function of borax concentration and holding temperature.

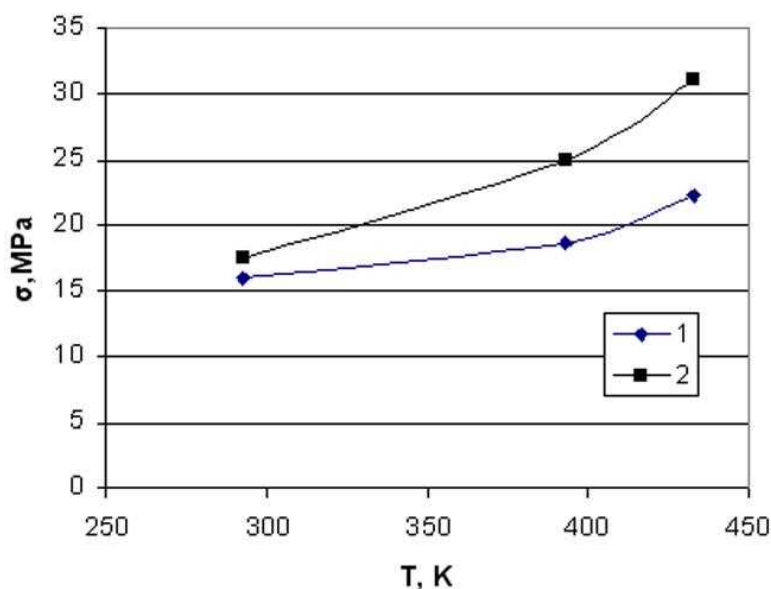


Fig.1. Variation of the tensile stress of films (1 - 5% borax, 2 - 10% borax) with borax concentration and temperature.

Conclusions

1. The obtained biodegradable films based on synthetic polyvinyl alcohol, Polyviol 6 04/140, containing corn starch, glycerin, and borax are transparent, homogeneous, and relatively thin. Elongation at break within 180 – 270 % is an important property for them for possible use as biodegradable packaging.

2. The study of the physical and mechanical characteristics of films with 5% and 10% borax content showed better tensile stress results with a higher content (10%) of borax.

3. The exposure of the studied film materials to temperatures of 393 K and 433 K improves their mechanical strength. To optimize the physical and mechanical properties of biodegradable film materials, the addition of borax is more appropriate than heat treatment from the point of view of resource efficiency.

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Processing of Petroleum-Containing Waste by Low-Temperature Pyrolysis Method

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Abstract. *The paper presents the results of the low-temperature pyrolysis of the most common petroleum-containing wastes, such as used oils and petroleum sludge, generated in oil production. The properties of pyrocondensate and the narrow fractions separated from it were studied. The obtained narrow fractions of pyrocondensate are proposed to be used in producing motor fuels.*

Keywords: petroleum-containing waste, used oil, petroleum sludge, pyrolysis, pyrocondensate.

Introduction

Petroleum-containing waste is among the most hazardous industrial waste types. It is generated as a result of industrial activities related to oil extraction, transportation, and refining, as well as during the routine operation of various machines and mechanisms that utilize lubricating materials. On the one hand, petroleum-containing waste contributes to environmental pollution, while on the other hand, it serves as a valuable source of hydrocarbons for various applications.

Used oils, which are produced in significant quantities during oil replacement procedures for different purposes, are often not efficiently utilized. The currently known methods for processing used oils include combustion, regeneration for reuse, and secondary processing to obtain additional amounts of boiler fuel or as supplementary components in heavy petroleum fuels [1,2]. Petroleum sludge is a complex mixture consisting of an organic fraction (petroleum products), mechanical impurities (clay, metal oxides, sand), and water. Petroleum sludge is primarily generated during crude oil extraction and, to a lesser extent, during its processing and transportation. In most cases, petroleum sludge accumulates in specialized pits or storage ponds, posing serious environmental risks by contaminating the air and groundwater.

Most existing petroleum sludge disposal technologies involve separating the organic fraction using mobile three-phase centrifuges, followed by its processing at oil refineries. Although thermal decomposition and coking of the organic fraction of petroleum sludge are known methods, they remain insufficiently studied and underutilized [3]. For this reason, the study of low-temperature pyrolysis as a method for obtaining feedstock for motor fuel production is a particularly relevant direction in the processing of petroleum-containing waste.

Results and Discussion

In this study, we utilized two of the most common types of petroleum-containing waste: used motor oil of the M-10DM grade and the organic fraction of petroleum sludge generated during oil extraction at the Boryslav oil field.

The low-temperature pyrolysis of petroleum-containing waste was conducted at a temperature of 420 °C. As a result of pyrolysis, pyrocondensate – a liquid product with a broad

fractional composition was obtained, along with a solid residue in the reactor and pyrolysis gases (Table 1).

Table 1

Material Balance of Low-Temperature Pyrolysis of Petroleum-Containing Waste

Raw Materials and Products	Mass Fraction, % for the Sample	
	Used Motor Oil M-10DM	Organic Fraction of Petroleum Sludge
Input: Petroleum-containing waste	100,0	100.0
Output:		
Pyrocondensate	92.5	85.5
Residue	2.3	8.3
Gas and losses	5.2	6.2
Total	100.0	100.0

The target product of the pyrolysis process of petroleum-containing waste – pyrocondensate is a transparent, light brown liquid with an odor characteristic of thermal decomposition products (Table 2). The high iodine number of the pyrocondensate indicates a significant presence of unsaturated hydrocarbons. Additionally, pyrocondensate is characterized by a low flash point, which prevents its use as furnace or boiler fuel, and a low pour point.

Table 2

Characteristics of Pyrocondensate from the Pyrolysis of Petroleum-Containing Waste

Indicator	Value for Petroleum-Containing Waste	
	Used Motor Oil M-10DM	Organic Fraction of Petroleum Sludge
Appearance	light brown liquid	
Density, kg/m ³	841.0	849.2
Refractive index	1.4728	1.5116
Sulfur content, wt. %	0.10	0.77
Pour point, °C	–18	–5
Flash point,		
in an open cup, °C	53	54
in a closed cup, °C	31	29

For the purpose of conducting research and determining the feasibility of using pyrocondensate from the pyrolysis of petroleum sludges for the production of motor fuels, it was divided into fractions: pyrocondensate up to 200 °C, 200-350 °C, and the residue >350 °C.

It has been established (Table 3) that the fraction up to 200 °C is characterized by a slightly heavier fractional composition. The sulfur content in this fraction exceeds the requirements set for commercial automotive gasoline. Additionally, this fraction exhibits a relatively high content of unsaturated hydrocarbons, as indicated by its high iodine number. For the potential use of this fraction as a component of commercial automotive gasoline, hydrofining must be carried out, which includes the hydrogenation of unsaturated hydrocarbons and hydrodesulfurization to reduce sulfur content. Subsequently, it is advisable to process this fraction in a catalytic reforming unit to increase its octane number.

Table 3

Characteristics of the Gasoline Fraction of Pyrocondensate from the Pyrolysis of Petroleum-Containing Waste

Indicator	Value for Petroleum-Containing Waste	
	Used Motor Oil M-10DM	Organic Fraction of Petroleum Sludge
Appearance	Transparent liquid of light yellow color	
Pyrocondensate yield, wt. %	13.6	22.9
Density, kg/m ³	742	751
Refractive index	1.4315	1.5087
Sulfur content, wt. %	0.02	0.384
Iodine number, g I ₂ /100 g	74.8	68.7

It has been established (Table 4) that the 200-350 °C fraction of the pyrocondensate obtained from the pyrolysis of petroleum-containing waste is characterized by a high flash point, meeting the requirements for diesel fuels. The low-temperature properties, defined by cloud point and pour point temperatures, are sufficient for utilizing this fraction in the production of summer diesel fuels. However, the excessively high sulfur content and the presence of unsaturated hydrocarbons require reduction, necessitating additional processing stages for this fraction.

Table 4

Characteristics of the Diesel Fraction of Pyrocondensate from the Pyrolysis of Petroleum-Containing Waste

Indicator	Value for Petroleum-Containing Waste	
	Used Motor Oil M-10DM	Organic Fraction of Petroleum Sludge
Appearance	Transparent liquid of dark yellow color	
Pyrocondensate yield, wt. %	25.1	58.7
Density, kg/m ³	834	843
Refractive index	1.4645	1.5167
Iodine number, g I ₂ /100 g	62.1	61.3
Sulfur content, wt. %	0.05	0.520
Cloud point temperature, °C	−12	−8
Pour point, °C	−20	−15
Flash point in a closed cup, °C	72	73

The diesel fraction of the pyrocondensate obtained from the pyrolysis of petroleum-containing waste is also advisable to be directed to hydrotreatment. After this process, the fraction can be used as a component of commercial diesel fuels. It should be noted that the additional processing of both the gasoline and diesel fractions of the pyrocondensate can be carried out in a mixture with gasoline and diesel fuel obtained from petroleum refining at oil refineries.

The >350 °C residue after the distillation of pyrocondensate (Table 5) is a highly viscous product that also contains a significant amount of unsaturated hydrocarbons. It can be added in small quantities to fuel oils. Another potential application of the residue is in the production of various types of lubricating greases, particularly conservation greases. However, this method of utilizing the residue requires further research.

Table 5

Characteristics of the Residue from the Distillation of Pyrocondensate from the Pyrolysis of Petroleum-Containing Waste

Indicator	Value for Petroleum-Containing Waste	
	Used Motor Oil M-10DM	Organic Fraction of Petroleum Sludge
Appearance	Viscous liquid of brown color	
Pyrocondensate yield, wt. %	63.3	18.4
Density, kg/m ³	871	917
Refractive index	1.4835	1.5312
Sulfur content, wt. %	0.114	1.473
Iodine number, g I ₂ /100 g	44.3	49.7
Pour point, °C	−11	+14
Flash point in an open cup, °C	215	128

Conclusions

The fundamental feasibility of processing petroleum-containing waste using the low-temperature pyrolysis method has been established, yielding pyrocondensate suitable for motor fuel production.

Low-temperature pyrolysis of petroleum-containing waste was conducted at 420 °C, resulting in the formation of 85.5-92.5 wt.% pyrocondensate, 2.3-8.3 wt.% solid residue, and 5.2-6.2 wt.% pyrolysis gas.

It has been determined that the light fractions obtained from the separation of pyrocondensate can serve as feedstock for the production of commercial motor fuels. The residue from pyrocondensate separation can be used as a component of fuel oil or an additive for lubricating greases.

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Study of Mechanical Properties of Starch-Based Biodegradable Films and Their Degradation Under UV Radiation

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Abstract. *This study examines the degradation of starch-based biodegradable films under UV radiation, focusing on their mechanical properties. Tensile strength and elongation were measured after different UV exposure durations. Results show a decrease in both properties, indicating material degradation, emphasizing the necessity for further research to enhance the stability of these films.*

Keywords: biodegradable films, starch, organic waste, strength, degradation, UV radiation.

Introduction

Environmental pollution from plastic waste, particularly petroleum-based packaging, is a critical ecological concern. Conventional plastics like polyethylene and polystyrene can take 400 to 1000 years to decompose, leading to microplastic formation and subsequent contamination of water, soil, and the food chain. This necessitates the development and use of environmentally friendly alternatives, such as biodegradable materials that decompose rapidly and harmlessly in natural environments.

Compared to other alternative materials, biodegradable films have a range of advantages and disadvantages. For example, partially degradable polymers or bioplastics derived from plant resources may possess some properties similar to those of biodegradable films, but they do not always degrade as quickly or are not as effective under real-world conditions. Partially degradable polymer films can leave microplastics in the environment, which poses a significant ecological challenge. In contrast, starch-based biodegradable films can degrade much more rapidly under the influence of microorganisms, minimizing their negative environmental impact. However, these films may be less resistant to mechanical damage and moisture, limiting their use in certain applications. On the other hand, bioplastics made from vegetable oils or other natural polymers may have better mechanical properties, but their production requires significant resources and may be less environmentally friendly due to the extensive land areas needed to grow raw materials.

Biodegradable materials can significantly help reduce plastic waste entering ecosystems. Reducing the amount of non-biodegradable plastic packaging materials is a crucial step in combating environmental pollution, especially in the context of global initiatives such as the fight against microplastics.

Starch-based films offer a promising solution. They can degrade within months due to microbial action or composting [1, 2]. Starch is readily available and inexpensive, making it an attractive option. These films are typically composed of polysaccharides like amylose and amylopectin, and their properties are influenced by the starch source [3].

Common starch sources include corn, potato, rice, tapioca, and wheat, each with unique physicochemical properties. Corn starch, for example, has a high amylose content (25-28%), providing excellent oxygen barrier properties, suitable for packaging [4]. However, plasticizers like glycerol are often added to enhance the strength and flexibility of these films [5].

The combination of PVA with starch improves the mechanical properties of films, such as tensile strength and water resistance [6]. Studies [7, 8] have shown that films based on polyvinyl alcohol exhibit good mechanical properties and are biodegradable.

Lviv, Ukraine, established its first municipal composting station in June 2020 [9], a significant step towards centralized organic waste processing. Despite this initiative and the increasing demand for eco-friendly materials, improper disposal of non-biodegradable polymer bags in organic waste containers remains a problem. Furthermore, "biodegradable" labels on commercially available bags are not always indicative of their actual decomposition rate and completeness.

This study aims to evaluate the mechanical properties and degradation of biodegradable bags sold in Lviv supermarkets. The objective is to assess their strength and verify manufacturers' claims regarding decomposition within six months. Given the common practice of disposing of these bags with organic waste, the research investigates their suitability for this purpose based on their degradation behavior.

Methodology

A universal tensile testing machine (dynamometer) with a 40 mm clamp distance was used to determine the mechanical properties of the films [10]. Tensile load tests were conducted at room temperature to measure elasticity, tensile strength, and mechanical load capacity.

To simulate natural sunlight, a fluorescent UV lamp was used, following the methodology in [11]. The distance between the lamp and the samples was 30 cm. Films were exposed to UV radiation for 3, 6, 9, and 12 hours.

Results

The mechanical properties of commercially available biodegradable films, marketed as eco-friendly replacements for traditional plastic bags, were analyzed. Examining their behavior under UV radiation helps assess their resistance to environmental factors and their effectiveness in real-world applications.

Table 1 presents the mass and thickness of the films, parameters that can influence mechanical testing results.

The sample with the lowest mass is produced by the company "Hrod-Haus" (11.68 g/m²), while the highest mass is recorded in the film from "Komserv Ukraine" (14.57 g/m²). This indicates variability in the density of the films, which may be due to differences in material composition or production technology.

The thickness of the examined films ranges from 9.0 to 9.7 µm. The thickest film is produced by "CA/SC Promateris SA" from Romania (9.7 µm). Ukrainian manufacturers maintain approximately the same thickness, ranging from 9.0 to 9.3 µm.

Table 1

Key parameters of biodegradable films

Sample No.	Manufacturer, Country	Mass, g/m ²	Thickness, µm
1	LLC «Hrod-Haus» Ukraine	11.68	9.0
2	Private Enterprise «Nika Plast» Ukraine	12.78	9.0
3	LLC «Komserv Ukraine» Ukraine	14.57	9.3
4	«CA/SC Promateris SA» Romania	13.25	9.7

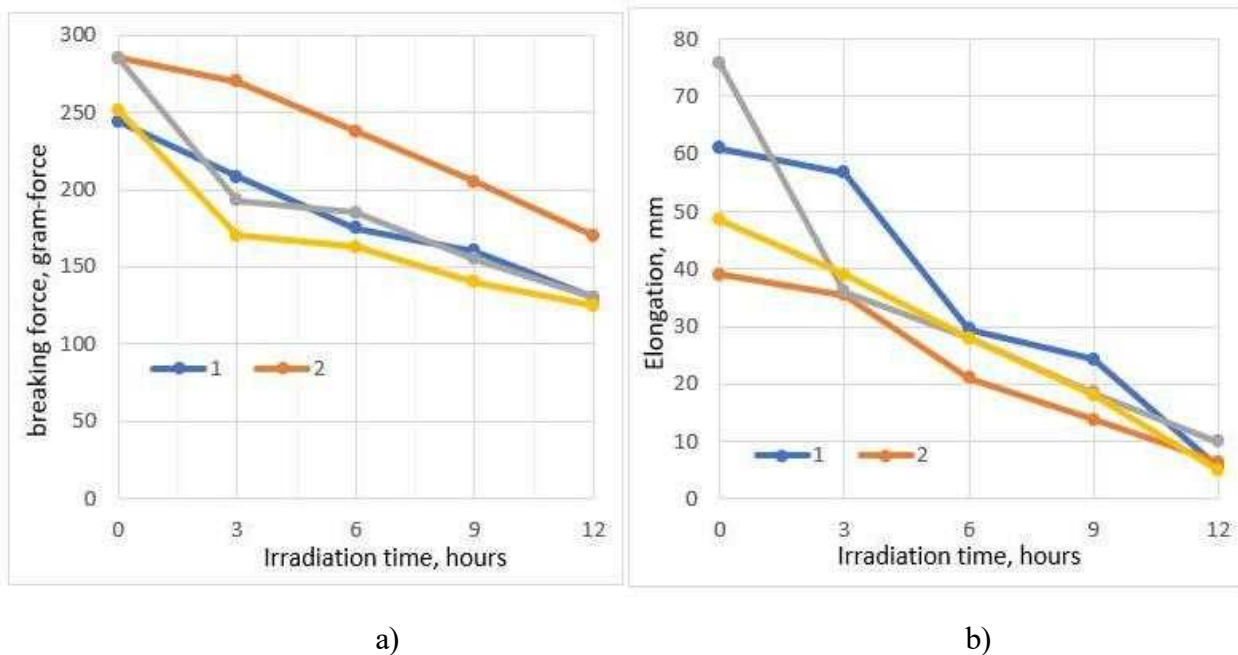


Fig. 1. Changes in mechanical properties of films in the longitudinal direction.

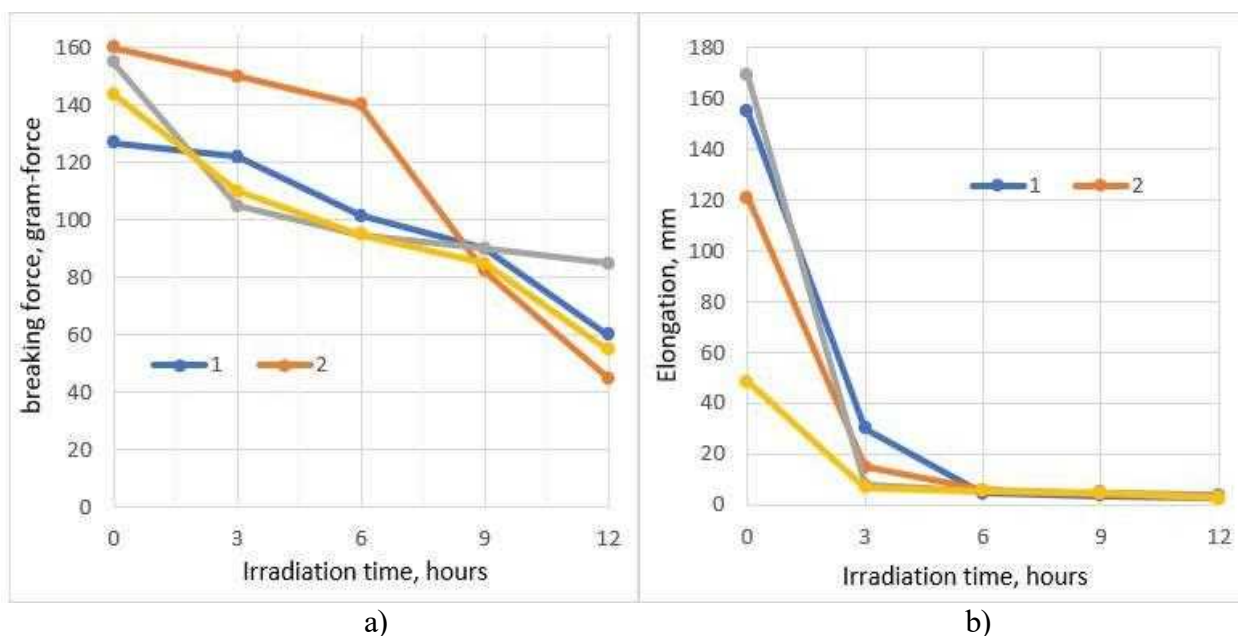


Fig. 2. Changes in mechanical properties of films in the transverse direction.

Figure 1 shows moderate reductions in the mechanical properties of the films in the longitudinal direction under UV radiation. The films exhibited greater strength in this direction, resulting in slower reductions in tensile strength and elongation compared to the transverse direction. Increasing irradiation time led to decreased tensile force and elongation, indicating material degradation. The most significant decrease was observed after 12 hours of irradiation.

Figure 2 shows the changes in tensile force and elongation in the transverse direction. Sample 3 showed a rapid decrease in tensile force within the first three hours, followed by a slower rate of decline, suggesting limited further degradation. Samples 1, 2, and 4 exhibited a consistent degradation rate, with similar properties after 12 hours. For elongation in the transverse direction, the most significant reduction occurred within the first three hours, stabilizing at a minimum (2.5-4 mm) after six hours for all samples.

Conclusions

The observed changes in mechanical properties under UV radiation demonstrate the degradability of these films, supporting their potential use as biodegradable materials. The most significant degradation occurred after 12 hours, highlighting the need for further research to improve material stability. The differing degradation rates observed in the longitudinal and transverse directions are important considerations for optimizing these materials for practical applications. These findings provide a basis for future studies aimed at enhancing the mechanical properties of biodegradable films exposed to UV radiation. Ukrainian manufacturers maintain high-quality standards, ensuring their products meet or exceed international benchmarks for film performance.

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**THE INNOVATIONS,
NANOTECHNOLOGIES, AND
CATALYSIS IN THE CHEMICAL AND
FOOD INDUSTRIES**

Study of Gas-Dynamic Throttle Elements as Sensors for Nanotechnology Processes

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Abstract. *On the basis of experiments for air, the dependence of the flow coefficient α of the watchstones as throttles on the diameter of their passage hole was obtained. The deviation of the calculated value of α from the experimentally determined value is 0.45 %. Also, for a throttle with a diameter of 0.083 mm, the dependence of α for different types of gases was obtained. The use of the obtained dependencies will improve the characteristics of the designed sensors for nanotechnology process control systems.*

Keywords – micro gas flow rate, gas-dynamic flowmeter narrowing device, watchstone, flow coefficient, diameter of the passage hole.

Introduction

Sensors are essential components of any cyber-physical system, including nanotechnology process control systems [1-3]. In chemical technology processes and various industries, for example, in gas-analytical instrumentation, the proper functioning of the respective systems requires a number of tools designed to both set and measure small and micro flow rates of various gases, absolute pressures and their differences, and the synthesis of complex gas mixtures of a given composition [4-11]. Such devices use gas-dynamic throttles as sensors – turbulent (nozzles, diaphragms) and laminar (glass or metal capillary pipes). The design of modern devices using such gas-dynamic throttles requires their further experimental study, since on the basis of the obtained results, new dependencies that are necessary for the construction of accurate mathematical models of modern gas-dynamic devices can be determined.

Among the special problems that arise in the process of developing control systems for the latest technological processes is the setting and measurement of small and micro flow rates of gases, in particular, in the production of fiber optics, integrated circuits, and medicine, nanotechnology, and energy, in particular, when controlling the composition of flue gases [12-17].

I. Purpose and objectives of the research

The main goal of the research is to minimize the error in constructing the static characteristic of turbulent throttle elements by establishing an accurate analytical dependence of the throttle flow coefficient α on the diameter d of the passage channel based on experimental data obtained using a flow measuring installation that implements the film method of gas flow measurement.

To achieve the goal, we will adhere to the following tasks:

- to obtain accurate experimental flow rate features of throttle elements of various types and different gases;
- to determine the value of the flow coefficient α for each standard size of the tested on different gases throttle and, based on the least-squares method, plot graphs of the dependence of the flow coefficient α on the diameter d of the passage channel of the throttle and on the type of gas (molecular weight M).

II. Research related to this issue

In this paper, turbulent throttle elements were studied, one of the important advantages of which is the possibility of applying them as primary measuring transducers of small and micro flow rates of gases, as well as for the synthesis of gas mixtures and dosing a wide range of industrial gases in the range of small and micro flow rate.

Our research has shown that in terms of stability and linearity of the calibration characteristic, as well as measurement accuracy, devices for measuring micro-flow rates of gases that implement the gas-dynamic throttle method of measurement, i.e., the variable differential pressure method, are promising. Watchstones with through-holes and capillary pipes are used as the primary measuring transducers of gas-dynamic micro flowmeters, which are narrow devices [19].

A well-known work [19] is dedicated to the study of turbulent throttle elements for the construction of a system of dosing elements based on gas-dynamic nozzles. This system of 6 connected in parallel nozzles is designed to set the flow rate of gas in multiples of 2, 4, 8, and 16 to the throttle taken as the basic one. However, the flow rate through the basic nozzle is determined with an error of 1 %, which does not ensure the construction of high-precision gas-dynamic devices (meters of small and micro flow rate of gases, synthesizers of gas mixtures) built on their basis.

To reduce the influence of random errors, the construction of calibration curves is performed based on the least-squares method, for instance, as it was implemented in [20] for the calibration of natural gas composition analyzers. However, only appropriate processing of experimental data cannot provide highly accurate final results if measurements are made with relatively large errors. Therefore, the construction of high-precision equipment based on precision primary transducers, in particular, for the calibration of gas micro flowmeters, is relevant.

III. Watchstones as measuring transducers for gas microflow rates

The use of watchstones with through-holes as narrowing devices for gas-dynamic throttle micro flowmeters for measuring gas micro flow rates is considered. The relative area m of such narrowing devices reaches values of the order of 0.001, and micro flow of gas G in this case is determined by the absolute pressures P_1 and P_2 before and after the watchstone.

The measured flow of gas G by a gas-dynamic micro flowmeter with a watchstone as a narrowing device is determined by the equation [20]

$$G = \alpha \cdot f \cdot (2 \cdot \rho \cdot \Delta P)^{0.5} \cdot (P_2/P_1)^{0.5/\kappa}, \quad (1)$$

where G – the mass flow rate of gas; α – flow coefficient; f – the area of the passage hole of the watchstone; ρ – gas density to the narrowing device; κ is the gas adiabatic index; $\Delta P = P_1 - P_2$.

The flow coefficient α , included in the flow equation of such a narrowing device, depends both on the controlled gas, the type of dependence $G=f(P_1, P_2)$, the Reynolds number Re , and on the value of the diameter d of the passage hole of the watchstone. The diameter d of such stones, depending on the size, ranges from 0.07 to 2.2 mm, and the deviation d from its nominal value can reach 5.0 %. Accordingly, the values of the coefficient α for watchstones of different sizes and of the same type differ among themselves. This leads to significant errors when measuring small and micro flow rates of gases using gas-dynamic flowmeters with watchstones as narrowing devices. The difference between α values for watchstones with diameters d in the range of only 0.08 to 0.11 mm reaches 9.5 %.

The flow coefficient α , which is included in the flow equation of the watchstone as a narrowing device of a gas-dynamic micro flowmeter, is determined experimentally using a flow

measuring device based on the film method of measurement with stabilization of the measured flow, the limit of the main relative error of which is 0.25 %. The flow measuring device is equipped with gas reducers, pressure stabilizers, manometers, thermometers, barometers, and a film flowmeter [21]. The procedure for determining the flow coefficient α of watchstones using such a flow measuring device is complex and time-consuming, since the study of the flow characteristic of the watchstone requires the use of high-precision instruments for measuring flow, pressure, and temperature, and stabilizing gas microflows, as well as gas flow parameters.

Therefore, there is a task to simplify and facilitate the procedure for determining the flow coefficient α of watchstones, in particular, to develop measures to determine an increased accuracy of the flow coefficient α of watchstones according to the value of the diameter d of their passage hole and, as a result, to increase the accuracy of measuring gas micro flow using gas-dynamic flowmeters with watchstones as narrowing devices.

The accuracy of measurement of gas-dynamic micro flowmeters with watchstones as narrowing devices (as it has been mentioned above) is determined both by the accuracy of measuring the pressures P_1 and P_2 before and after the watchstone, and by the accuracy of determining the flow coefficient α of such devices, the value of which depends on the diameter d of the passage hole of the stone. The value of the flow coefficient α is determined (as it has also been mentioned above) experimentally on the basis of the analyzed gas for a specific watchstone using a flowmeter, which is a rather complicated and time-consuming process. Therefore, the study of the dependence of the flow coefficient α on the diameter d of watchstones and the establishment of an analytical description of this dependence will make it possible to simplify the procedure and increase the accuracy of determining the coefficient α of a specific watchstone by the value of its diameter d , and, therefore, to increase the accuracy of measuring gas micro flow rates with such narrowing devices.

The accuracy of the flow equation of watchstones with through holes as primary measuring transducers of gas flow is established by experimental studies of such measuring transducers. The values of the coefficient α included in the flow equation (1), which has been mentioned above, differ among themselves both for stones of different standard sizes and stones of the same type. To establish the dependence of the coefficient α of the stone on its diameter d and the type of controlled gas, experimental studies of the flow characteristics of watchstones of different sizes and on the basis of different gases were conducted. Experimental studies were performed with the help of a flow measuring device, which implements the film method of gas flow measurement, and the limit of the basic relative error of which is 0.25 %. According to the obtained experimental data, the values of the flow coefficient α of the stones under investigation were calculated according to the flow equation (1). The results of these studies confirmed the dependence of the flow coefficient α for the flow equation (1) on the number of Re , the type of gas, and the standard size of the watchstone.

To establish the functional dependence $\alpha(d)$ of the studied turbulent throttle, a model flow measuring device was developed, the diagram of which is presented in Fig. 1. Its main element is the flowmeter 5, built on the basis of the film method of gas flow measurement with the main relative error of 0.25 %. The throttle element DE under investigation is fixed in the mandrel 6. At the DE output, an electromagnetic valve VI is installed, the "on-off" signal of which is given by the researcher-experimentalist using the MCU microprocessor unit. The metered gas from the source flows to the serially installed dehydrator and mechanical filter (not shown in the diagram), and then to the pressure stabilizer 1, from the output of which the gas passes through the chamber 7, in which the pressure sensor 2 is installed. Signals from sensors 2-4 are sent to the MCU , which

displays the measurement indicators of input excess pressure P_1 , atmospheric pressure P_0 , and the temperature T stabilized in the thermostat T_s , respectively. The MCU calculates the flow rate of the test gas according to equation (1) based on the measured parameters.

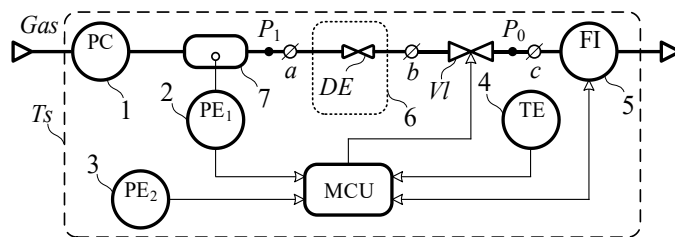


Fig. 1. Scheme of the flow measuring installation for experimental studies of the flow features of watchstones:

1 – regulator-target pressure; 2 and 3 – sensors for measuring input excess pressure P_1 and atmospheric pressure P_0 , respectively; 4 – metered gas temperature sensor; 5 – film flow meter; 6 – block for hermetic fastening of the tested throttle; 7 – a chamber for smoothing possible gas pressure pulsations and placing the sensitive element of sensor 2.

Therefore, the obtained values of the flow coefficient α of the studied watchstones calculated according to equation (1) based on the experimental flow characteristics of these stones for air differ significantly among themselves both for different standard sizes of stones and for different gases. Thus, the coefficient α in air in the range of Re number from 700 to 2700 for a watchstone with $d = 0.083$ mm is equal to 0.70, for a stone with $d = 0.093$ mm – 0.73, and for a stone with $d = 0.113$ mm – 0.77. The largest deviation of α of each of the given stones in the indicated Re number range does not exceed 1.3 %, and the difference between α values for different of these stones is 9.5 %. The graph of the dependence of the flow coefficient α on the diameter d of the passage hole for different standard sizes of watchstones for air is shown in Fig. 2.

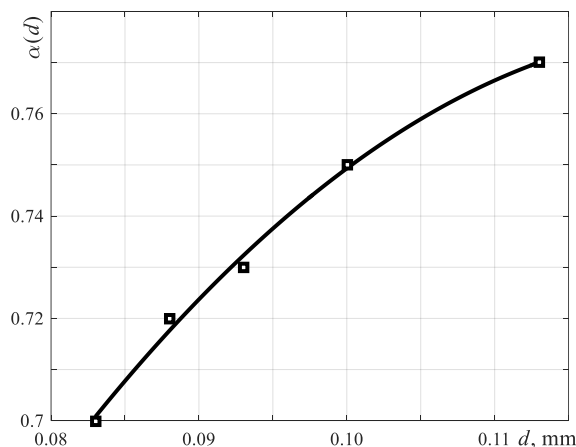


Fig. 2. Graph of dependence of flow coefficient α on the diameter d of the passage hole of watchstones for air.

The difference between the values of the coefficient α of watchstones for different gases is similar. For example, for a watchstone with $d = 0.083$ mm, the coefficient α for helium in the Re range from 200 to 500 is 0.63, and its largest deviation in this Re range does not exceed 3.2 %. For carbon dioxide, the same values and for the same stone in the range of Re numbers from 800 to 2500 are equal to 0.73 and 2.6 %, respectively. The graph of the dependence of the flow coefficient α on the type of controlled gas (molecular weight of the gas) for a watchstone with the diameter of its passage $d = 0.083$ mm is shown in Fig. 3.

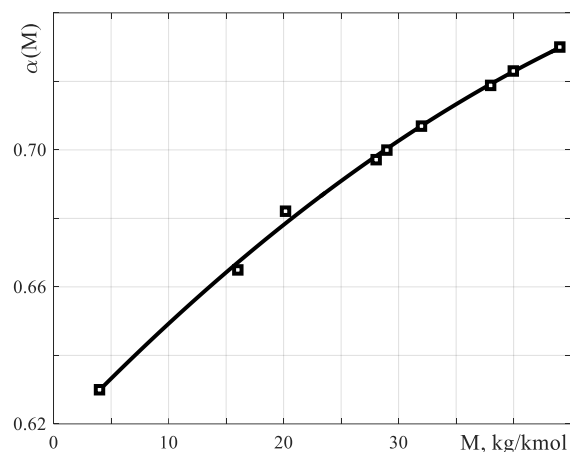


Fig. 3. Graph of dependence of the flow coefficient α of the watchstone with the diameter of the passage hole $d = 0.083$ mm on the type of controlled gas (molecular weight of the gas).

Due to the dependence of α of the watchstone flow coefficient on the factors considered, its value for a particular watchstone is usually determined experimentally based on the study of its flow characteristics using a flow measuring installation. Such a procedure for determining α of the watchstones is complex and time-consuming, and requires the use of high-precision devices for measuring and stabilizing micro-flow rates of gases

In this paper, based on the processing and analysis of the experimentally obtained values of the flow coefficient α of watchstones with different diameters d of their passage hole, an analytical description of the dependence of the coefficient α on the value of the diameter d of the watchstones in the form of a square polynomial is considered. This analytical dependence, for example, for watchstones with diameters d ranging from 0.08 to 0.11 mm for air, is as follows [22, 23]:

$$\alpha = a_2 \cdot d^2 + a_1 \cdot d + a_0, \quad (2)$$

where $a_2 = -41.9781$; $a_1 = 10.5357$ and $a_0 = 0.1155$ are the coefficients of the proposed quadratic polynomial, in which the diameter d of the passage hole of the studied watchstone is expressed in mm.

The deviation of the value of the flow coefficient α , determined according to dependence (2), from its value, determined experimentally, does not exceed 0.35 %. That is, this analytical dependence provides a high-precision calculation of the value of the flow coefficient α of a specific watchstone based on the particular value of its diameter d of the passage hole.

An analytical dependence of the flow coefficient α on the type of controlled gas (molecular weight of the gas M) for a watchstone with a diameter of its passage $d = 0.083$ mm is also provided. This dependence is as follows:

$$\alpha = b_2 \cdot M^2 + b_1 \cdot M + b_0, \quad (3)$$

where $b_2 = -0.2147 \cdot 10^{-4}$; $b_1 = 0.3529 \cdot 10^{-2}$ and $b_0 = 0.6161$ are the coefficients of the proposed quadratic polynomial, in which the molecular weight of the gas is expressed in kg/kmol.

The deviation of the value of the flow coefficient $\alpha(M)$, determined according to dependence (3), from its value determined experimentally, does not exceed 0.5 %.

IV. Results and discussion

Therefore, the application of the proposed analytical dependence of the flow coefficient α of watchstones on the diameter d of their passage hole provides a simplification of the procedure and an increase in the accuracy of determining the coefficient α based on the value of the diameter d of a specific watchstone as a narrowing device of a gas-dynamic micro flowmeter, i.e., it makes it

possible to significantly improve the accuracy of measuring small and micro flow rates of gases by using such flowmeters.

The deviation of the value of the flow coefficient α calculated according to the obtained analytical dependence (2) from the experimentally determined value for watchstones with diameters d in the range from 0.08 to 0.11 mm does not exceed 0.35 %, and the value calculated according to dependence (3) for a stone with $d = 0.083$ mm on various gases with a molecular weight ranging from 4 to 40 kg/kmol does not exceed 0.5 %.

V. Conclusions

1. On the basis of the developed high-precision installation, the flow rate features of gas-dynamic turbulent throttle elements (watchstones) for various standard sizes and different gases were obtained.

2. Analytical dependences were gained using the least-squares method to determine the flow coefficient α from the diameter d of the passage channel of the studied watchstones.

3. The use of such gas-dynamic resistances as narrowing devices of variable differential pressure flowmeters is promising for the construction of high-precision gas-dynamic flowmeters of small and micro flow rates of both individual gases and gas mixtures.

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Innovative Techniques For Producing Yogurts With Increased Nutritional Value

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Abstract. Fermented milk products of this line are becoming more popular with consumers and are expanding the range of fermented milk products in the segment of kefir, fermented baked milk, yogurt, cheese, and cream drinks. According to the results of most assessments, the optimal ratio of 30% by weight of quinoa for obtaining fermented milk yogurt with the most satisfactory characteristics has been determined. A health product is proposed, which is included in the diet of the main population groups and may have medicinal properties.

Keywords: yogurt, fermented milk product, quinoa, milk, starter culture, stevia extract, technology.

Introduction

The food industry is becoming increasingly important as an important component of the human health system and occupies a priority place in the formation of its intellectual potential and social activity. New food products must meet the requirements of modern nutrition and provide the population with affordable health (functional) products, since the state of human health directly depends on the structure and quality of nutrition. In Ukraine, the level of consumption of many food groups does not meet the rational norm. First of all, this applies to products of animal origin, which causes an imbalance in the ratio of proteins, macro- and micronutrients. In the daily diet, the following products predominate and significantly exceed the norm: oil (177 %), potatoes (148 %), bread and bakery products (123 %), sugar (130 %). Approximately 50–60% of Ukrainians have an unbalanced diet. Violation of the diet significantly contributes to the development of a number of diseases, especially those of the circulatory system. Inadequate nutrition is also a significant risk factor for the development of digestive diseases. The main characteristics of an unbalanced diet that contribute to the development of diseases include: excessive consumption of foods high in total fat, saturated fatty acids, cholesterol, as well as refined sugar, salt, and alcoholic beverages; insufficient mono- and polyunsaturated fatty acids, complex carbohydrates, dietary fiber, antioxidant vitamins, and mineral elements important for metabolism. Functional products include primarily fermented milk products with an appropriate composition of microflora and essential nutrients.

The dairy industry is one of the most important in the economy of Ukraine and in food production in general. Ukrainian dairy enterprises, in terms of production in 2020, ranked sixth in the world and were among the largest exporters of dairy products. The global market situation has always contributed to their production: a constant increase in prices stimulates an increase in production volumes, and the growth of the population contributes to their preservation in the long term. In Ukraine, in recent years, yogurt has become one of the most common fermented milk products. Dessert yogurts, as well as drinking and organic yogurts, are especially popular. For the first time, these fermented milk products appeared in the early 90s in large cities, mainly of Polish production and other countries, and did not raise great prospects for introduction into production to diversify the range of dairy products in Ukraine. Until 2000, their share among fermented milk products was less than 5% of all dairy products. Today, yogurts have replaced many fermented

milk products, as they play an important role in ensuring and supporting human life; in the overall structure of Ukrainian production today, they occupy up to 20% among dairy products [1 – 4].

Since the beginning of the 21st century, the problem of functional products based on fermented milk raw materials has become increasingly popular. The Ukrainian yogurt market is constantly developing, which allows us to keep consumers in good shape without reducing interest. Today, quite a lot of work is being done to produce yogurts with various ingredients that have biologically active properties. Therefore, expanding the line of such products by introducing plant food components will enrich and improve their characteristics and increase the assortment. Every day, the population is becoming more aware of the fact that most problems related to nutrition can be overcome by changing the daily diet. Fermented milk products are products of high biological value and are able to balance it [5–10].

There are several varieties of quinoa, which differ in color and flavor, but have a light nutty flavor and are great for combining with various products to prepare a variety of dishes. White quinoa has a more delicate and delicate taste, similar to porridge, and cooks well. Black quinoa is slightly sweeter than red, and both are firmer in texture, so they perfectly complement snacks. This cereal is rightly called a superfood; its composition surpasses many traditional cereals: rice, corn, and millet. Quinoa consists of 70% carbohydrates (it does not contain gluten, so people with gluten intolerance can use it as an alternative), 15% protein (all essential amino acids, so it is recommended as part of a vegetarian diet. On the other hand, quinoa has a large composition of vitamins B, A, C, and E, as well as essential fatty acids and a set of micro- and macroelements represented by a rich composition: potassium, magnesium, sodium, phosphorus, iron, manganese, and copper. Quinoa contains a significant amount of dietary fiber, which stimulates intestinal function, normalizes glucose, insulin, and cholesterol levels, as a preventive measure against cardiovascular diseases and diabetes. Quinoa contains active compounds quercetin and kaempferol, the so-called flavonoids, with antioxidant properties, and has antidepressant, anti-inflammatory, antiviral, and anticancer effects. Moreover, the amount of quercetin in quinoa is even higher than in typical products, with its high content, for example, cranberries. With regular use, quercetin accumulates in the body, gradually increasing the strength of its beneficial effects. In general, white quinoa contains more iron, red fats, and proteins, and only black is considered dietary.

Experimental results and discussion

Expanding the range of functional fermented milk products for specific segments of the population, vegetarians, and improving technology with minimal changes to existing production. The object of research is the technology of producing a fermented milk product using the superfood quinoa. The subject of research is samples of fermented milk products with different contents of quinoa superfood, based on cow's milk (DSTU 2661:2010) and the starter "Yogurt Vivo" (TUU 15.5- 3060300036-001:2009), which contains standardized for industrial production strains of lactic acid streptococci *Streptococcus thermophilus*, Bulgarian bacillus *Lactobacillus bulgaricus* and acidophilus bacillus *Lactobacillus acidophilus*, dry stevia extract (TUU 10.8-34352680-003-2015) as a natural sugar substitute and preservative, which has antimicrobial and antifungal properties.

The primary requirement from the consumer is attractiveness and organoleptic evaluation. Pasteurization of dairy raw materials was carried out under the following heat treatment regimes: 100 °C without holding; 85 °C with holding for 5 – 6 min.; without heat treatment. Yogurt production was carried out using the following technology: pasteurization, cooling to a temperature of (36 ± 1) °C, fermentation, and cooling. The fermentation process was carried out

in a Moulinex YG230 household yogurt maker. The organoleptic and physicochemical indicators of the raw materials were studied using standard methods. During the fermentation process, titrated acidity was controlled. In the finished products, organoleptic indicators, titrated acidity, and degree of syneresis (by filtration) were studied. Classical studies of the production of fermented milk beverages have revealed the fact that an increased temperature of heat treatment of raw materials improves their organoleptic properties and ability to retain moisture [11 – 13, 15]. When using pasteurized drinking milk as a dairy raw material, the resulting products had a taste and aroma characteristic of yogurt. However, samples produced using heat treatment regimes had consistency defects that increased in proportion to the increase in the pasteurization temperature. Yogurt obtained from raw materials pasteurized at a temperature of 100 °C had a floury consistency with whey separation. The best consistency and organoleptic evaluation was in the product without heat treatment. The degree of syneresis in samples with heat treatment increased in proportion to the increase in temperature: from 30 to 45%, respectively. A slight stratification was observed due to a decrease in the mass fraction of fat in milk from 3.5 to 1.5%, and a slight separation of whey was observed. Syneresis research revealed that at high pasteurization temperatures, the degree of syneresis increases from 60 to 80%. A general analysis of the course of fermentation processes revealed that temperature treatment affects the duration of the process. With an increase in temperature regimes, fermentation processes are accelerated to 1 hour. When using heat treatment modes for pasteurized milk, the time during which the acidity reached the standard value for yogurts 80 T was 6 hours; for untreated, 5.0 hours, respectively. When using pasteurized drinking milk for the production of yogurt at home, repeated heat treatment is impractical, as it worsens the quality of the finished products. When using raw milk, the optimal pasteurization modes are heat treatment at 85 °C with a holding time of 5 – 7 minutes, which will ensure the production of a high-quality product. The duration of fermentation is inversely proportional to the temperature of heat treatment.

Table 1

Main physicochemical parameters of experimental samples

Indicator	sample	10 %	20 %	30 %	40 %
Active acidity, pH	4.8	3.9	4.5	4.9	3.9
Titrated acidity, T	90	115	130	140	133
Viscosity, Pa·s 10 ⁻³	0.77	0.69	0.75	0.79	0.82
Volume holding capacity, %	89	91	93	96	93

The results of the studies (see table) showed that the quinoa content of more than 30% has little effect on the organoleptic characteristics of fermented milk yogurt; the difference occurs for different types of milk in terms of chemical composition, so for skimmed milk, these indicators are the lowest. To improve the taste properties and maximize the preservation of naturalness, it is proposed to add stevia in the form of a finely dispersed powder. A food sugar substitute is added to the mixed and partially cooled curd, and mixed until they are evenly distributed. Uniform distribution is ensured due to the water-holding capacity during intensive mixing. To substantiate the method of introducing the food enricher, two methods of introduction were studied: I involved the introduction of the enricher mixture at the fermentation stage, II - after fermentation at the mixing stage, and its type - dry powder and in the form of an aqueous extract. As a result of the experiment, it was found that the introduction of a mixture of food fortifiers at the stage of fermentation and souring in the form of an aqueous extract led to a slow increase in acidity, the clot formed poorly, and in some cases did not form at all. Stevia, in the form of powder, contains a complex of biologically and physiologically active substances and does not change the structural features of the fermented milk product much. Since the chemical composition of stevia includes steviosides, amino acids, carotenoids, vitamins, flavonoids, as well as macro- and microelements,

which increase the functional properties of yogurt and do not worsen the main characteristics of yogurt for 14 days. The high content of biologically and physiologically active substances in food additives can inactivate lactobacteria and delay the souring process. Therefore, the introduction of a food fortifier in the form of a mixture with syrup, after cooling and mixing the clot, allows you to obtain a product with the specified properties.

Conclusions

A technology for the production of new types of functional products – enriched yogurts in laboratory conditions has been developed, technological schemes have been drawn up, and a technology for the production of products on an industrial scale has been proposed. Fermented milk products of this line are becoming more popular with consumers and are expanding the range of fermented milk products in the segment of kefir, fermented baked milk, yogurt, cheese, and cream drinks. According to the results of most assessments, the optimal ratio of 30% by weight of quinoa has been determined for obtaining fermented milk yogurt with the most satisfactory characteristics. A health product is proposed, which is included in the diet of the main population groups and may have medicinal properties.

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Study of the Wine Clarification Process with Bentonite

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Abstract. The fermentation of Isabella and Pocklington grape varieties was carried out to obtain dry wine materials. The process of treating wine materials with conventional bentonite and modified bentonite at the clarification stage was studied. It was found that the acidity of the wine materials systematically decreases by the end of the treatment when using modified bentonite. It is proposed to use modified bentonite samples in winemaking technology, as they not only contribute to clarification but also reduce the acidity of the wine.

Keywords: red wine, white wine, wine material, bentonite, modified bentonite.

Introduction

Wine stabilisation and clarification are important steps in the wine production process, during which turbidity can be eliminated or prevented while maintaining the quality of the drink. These measures are aimed at improving certain characteristics of wine and ensuring its quality and stability over time. The most widespread treatment of wines from a technological and economic point of view is the treatment with bentonite [1, 2]. Bentonite is a clay with a SiO₂ content of 50...65 % by weight, Al₂O₃ - 15...20 % by weight, Ca, Mg, Na, Fe oxides - 0.5...3.5 % by weight. In appearance, bentonite is a fine cereal or powder of grey or greyish-yellowish colour, tasteless and odourless; humidity is within 3...10 % by weight, and pH is 9 [3]. Bentonite has the ability to swell in water, i.e., it can form colloidal systems with pronounced adsorption properties of protein compounds that coagulate with increasing acidity. Bentonite clays are capable of adsorbing polypeptides, proteins, enzymes, amino acids, yeast, and bacterial cells. This property of bentonite clays is used in the technology of clarification of wines, juices, wine, and apple cider vinegar [3 - 5].

The adsorption of protein substances is based on the fact that most proteins in the wine material have a positive charge, while bentonite has a negative charge. Therefore, the opposite charge values of the particles lead to their adsorption. Coagulation and adsorption of bentonite occur very quickly, with protein compounds being separated almost completely, and wine microorganisms, within 80...90 % [6]. In the mechanism of wine clarification, a decisive role is played not only by adsorption processes, but also by the coagulation of molecules due to electrostatic interaction with bentonite particles and adhesive sticking to the surface of clarifier particles. The acidity of wine significantly affects the efficiency of its clarification: with an increase in the pH of the medium, the agglomeration rate of the bentonite suspension increases. During swelling, bentonite increases in volume by 8...10 times from the initial level (typical for bentonites with a high sodium content). Swelling is more efficient with an increase in the level of clay dispersion [3, 7].

At the same time, the treatment of wine material with bentonite can cause an increase in the content of calcium and its compounds by 46...68 mg/dm³. Calcium compounds in reactions with tartaric acid form calcium tartrate (CaC₄H₄O₆), which can cause crystal cloudiness. Therefore, wine materials should be treated with bentonite before cold processing.

When bentonite is used, the organoleptic characteristics of young white wines are improved, while those of aged wines are preserved. Red wine materials may slightly lose colour. The dose of bentonite is determined by trial treatment. The best option is the one that uses less bentonite and does not contain excessive protein. The recommended rate of bentonite use is in the range of 5...30 g/dal [8, 9].

To increase the efficiency of clarification, activated bentonite is used - chemically activated clays with basic properties that allow for the reduction of the level of acidity in wine through chemical interaction. In order to increase the adsorption capacity of bentonite, a 0.2 % sodium carbonate solution is used instead of water to prepare the suspension. The suspension is stored for no more than 5...6 days. A 5 % suspension of bentonite is fed into the wine material by constant stirring [3]. Alkaline activation is carried out by means of mechanochemical reactions with solutions of NaOH and Na₂CO₃ to increase the sodium content in bentonite clays and thus improve the above properties [10]. Accordingly, methods of modifying bentonite clays with acidic properties are also known. The reagents used were sulfuric acid, acetic acid (acid to clay ratio = 20, 40, and 60%), and a sulfuric-acetic mixture (1:1). Ordinary and modified bentonite clays are not only used in the food industry, but also for the purification of oil products [11]. In this work, we propose the use of ordinary and modified bentonite clay with agents with basic properties to clarify wine and, if necessary, reduce its acidity.

The aim of the research is to produce wine samples, clarify them by treating them with bentonite and activated bentonite, and study changes in the active and titratable acidity of the drink during the clarification process.

Research Results

Berries of the Isabella grape variety were used to make red wine, and Pocklington grapes were used for white wine. The berries were separated from the crests and from substandard and unripe berries, and mashed to obtain pulp. For red wine, the skins and seeds were not separated from the pulp; for white wine, the skins and seeds were separated. The pulp or juice was placed in containers so that the raw material occupied no more than 2/3 of the container capacity. The containers were closed with a water seal and left to ferment for a week. Next, for red wine, we separated the skins and berries, carefully poured the fermented wine material without sediment into clean containers, added sugar at the rate of 100 g per 1 litre of wine material, mixed, closed with a hydraulic seal, and left for secondary fermentation for a month. The resulting wine was clarified and then poured into airtight containers and sent for storage in a cool place.

Wine clarification with bentonite was carried out at the rate of 3 g/dm³ of young wine. The bentonite was preliminarily prepared by soaking in a 5-fold volume of hot water (50...60 °C) for 4 hours. After adding the bentonite suspension to the wine, it was stirred and settled.

For clarification, bentonite clays were used - aluminosilicates, mainly montmorillonite (over 75 %) and beidellite, commercial and activated with alkaline properties.

The titratable acidity was determined by sampling the wine, followed by automatic titration with a 0.1 N NaOH solution using an Easy Pro Mettler Toledo automatic titrator. The active acidity (pH) was determined by the potentiometric method using an automatic pH meter Mettler Toledo SevenCompact S220-Kit. The organoleptic characteristics of red and white wine were determined by quality indicators based on the standard list of attributes (properties) that most fully cover the main quality characteristics of the product (DSTU 4806:2007 Wines).

Physicochemical parameters were determined for the wines obtained using the methods described above. The results of the study are presented in Table 1.

Table 1

Physical and chemical parameters of the untreated wine material

	Red wine	White wine
Volume fraction of ethyl alcohol, %	6.9	7.5
Content of titratable acids in terms of tartaric acid, g/dm ³	9.51	12.0
Active acidity (pH)	3.55	3.19
Sugar content, g/dm ³	7.0	8.5

The organoleptic characteristics of unprocessed wine material are determined in accordance with DSTU 7209:2011 Unprocessed grape wine materials. General technical conditions. The results of the study are presented in Table 2.

Table 2

Organoleptic characteristics of untreated dry wine material

	Red wine	White wine
Colour	Intense red with various shades	Light straw, homogeneous
Aroma (bouquet)	Varietal, well-defined with a strawberry note, without foreign tones	Varietal, well-defined aroma of grape skins, without foreign tones
Taste	Clean, full, harmonious, without excessive astringency and off-flavours	Clean, full, harmonious, without excessive astringency and off-flavours

Wine produced from white grapes contains a lower percentage of ethyl alcohol, has a higher titratable acidity (in terms of tartaric acid), lower active acidity, and a higher content of unfermented sugars. The data indicate that in the case of must fermentation from white grapes, a greater amount of secondary fermentation products could be formed (initial grape sugar content of 17.2 %). In the case of red grapes (initial grape sugar content of 16.8 %), the titratable acidity is lower and the pH is higher.

Changes in titratable acidity of wine during the bentonite treatment process

Samples of white and red wine material were treated with conventional bentonite and modified bentonite in the amount of 3 g/dm³ of wine. The figures show the graph of changes in titratable acidity during the treatment with bentonite.

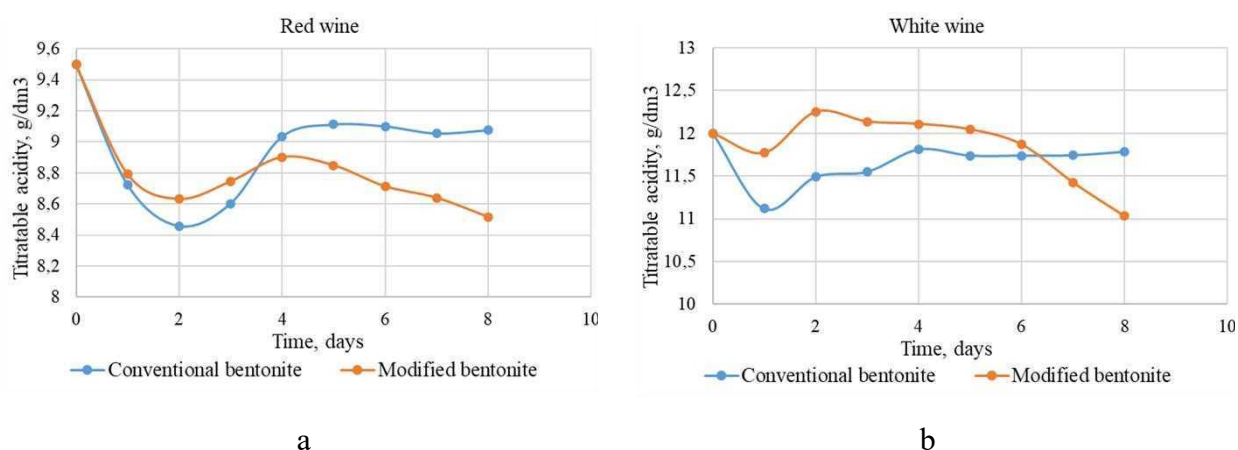


Fig. 1. Titratable acidity in the process of clarification of red (a) and white (b) wine material with conventional bentonite and modified bentonite.

A decrease in titratable acidity in terms of tartaric acid was observed in both samples when using modified bentonite as a clarifier.

In all samples of red wine material, a significant decrease in acidity was observed in the first two days of the experiment, then, when using unmodified bentonite, the acidity increased almost to the initial value (9.01 g/dm^3). When using modified bentonite, the titratable acidity of the wine material systematically decreases to a value of 8.51 g/dm^3 .

On the first day of clarification of white wine, a significant decrease in titratable acidity was observed, followed by its levelling off almost to the initial value when using ordinary bentonite and its decrease to 11.03 g/dm^3 from the sixth day when using modified bentonite.

Similar patterns were observed in the determination of active acidity. Fig. 2 shows the value of active acidity at the beginning of the experiment and after 8 days.

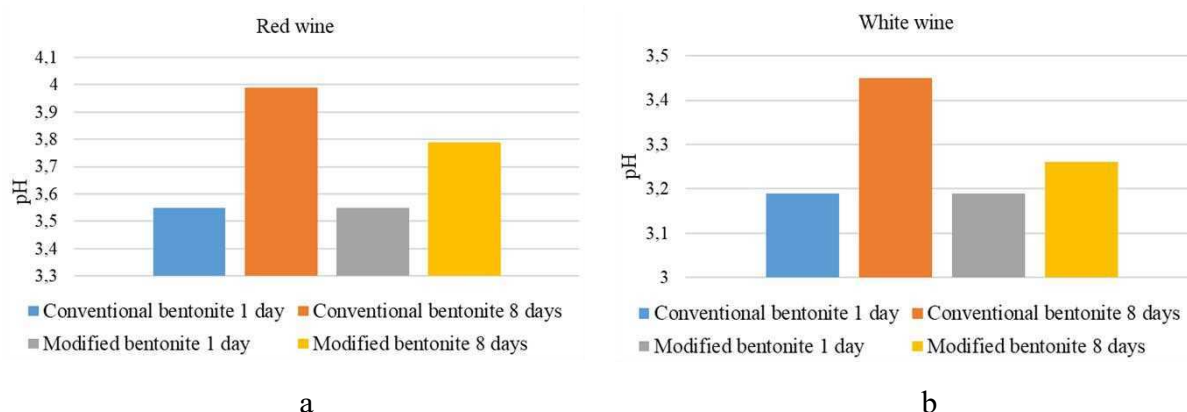


Fig. 2. pH of red (a) and white (b) wine material on the first and eighth day of the clarification process.

As can be seen from the data, the active acidity of wine at the end of the experiment is higher in samples using ordinary bentonite and slightly increases when using modified bentonite.

Conclusions

White and red samples of wine material were obtained by fermentation of Pocklington and Isabella grape varieties, and their physicochemical and organoleptic characteristics were determined. The wine material was treated with conventional and modified bentonites to clarify it. A significant decrease in acidity using common bentonite in red wine samples was observed in the first two days of the experiment, and then the titratable acidity increased almost to the original value (9.01 g/dm^3). The titratable acidity with the use of modified bentonite systematically decreases to 8.51 g/dm^3 . In samples of white wine with ordinary bentonite, the titratable acidity decreases significantly on the first day, and then practically levels out to the initial value. When clarified with modified bentonite, the titratable acidity decreases from the sixth day to 11.03 g/dm^3 .

As a result of the analysis of the obtained dependencies, it is proposed to use modified bentonite samples in wine technology as those that, in combination with clarification, reduce the acidity of wine, which makes it possible to improve its organoleptic characteristics. This technological technique is a good solution for the development of Western Ukrainian viticulture and winemaking, as it makes it possible to solve the problem of high acidity of zoned grape varieties.

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Sol-Gel Synthesis of Organic/Inorganic Materials with High Proton Conductivity

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Abstract. *Methods for the synthesis and modification of novel functional sulfo-containing polyacrylate materials have been developed. The use of sol-gel technology made it possible to obtain hybrid organic/inorganic materials with high structural homogeneity. The resulting nanocomposite materials are characterized by high proton conductivity and have promising applications in solid-state fuel cells as proton-conducting membranes.*

Keywords: organic/inorganic, sol-gel process, nanocomposite, proton conductive membrane, fuel cell, polyacrylate.

Introduction

The development of modern civilization requires the implementation of an energy transition, that is, a comprehensive restructuring of all sectors of the economy in order to stop using fossil fuels and completely switch to carbon-free technologies and energy-efficient consumption [1]. Fossil fuels, when burned, emit greenhouse gases that cause climate change on the planet. In addition, fossil fuel reserves are gradually being depleted.

In recent years, fuel cell technology has been considered to be a good alternative to traditional energy production and to play an important role in realizing a hydrogen-based society [2]. At present, proton exchange membranes used in commercial fuel cells are perfluorosulfonic acid polymer membranes (Nafion HP, Nafion XL, Gore-Select). For the purpose of improving their chemical and mechanical properties and extending the service lifetime, they are stabilized with antioxidative additives (for example, CeO₂) and reinforced with porous expanded polytetrafluoroethylene [3].

Different types of polymers have been investigated as promising alternatives to address high robustness and chemical stability, not compromising the fuel cell performance, including organic/inorganic composites. In [4], the authors reported the development of partially fluorinated sulfonated polyphenylenes reinforced with poly(vinylidene fluoride) (PVDF) nanofibers. The resulting composite membrane exhibited excellent chemical stability and stable rupture energy at high and low RH levels, allowing it to be an alternative proton-conductive membrane to meet the U.S. Department of Energy target to be used in automobile fuel cells in 2025.

One of the strategies to obtain a hybrid organic/inorganic membrane with desired characteristics is the use of sol-gel technology. Sol-gel phase introduced into the polymer matrix in a sufficient amount allows the membrane to reach the improved functional properties suitable for application in PEMFC. The study [5] explores a novel *in situ* synthesis method for PDMS/SiO₂ nanoparticle composites with varying cross-linking degrees (PDMS: TEOS of 15:1, 10:1, and 5:1); particle concentrations (5%, 10%, and 15%); and sol-gel catalysts (acidic and alkaline). PDMS/SiO₂ composites demonstrate tunable properties by controlling the sol-gel and crosslinking synthesis parameters.

In the present paper, we report the method of synthesis of the hybrid organic/inorganic composite material with proton conductivity for potential use in proton exchange membrane fuel cells (PEMFCs).

Sol-gel synthesis of organic/inorganic composites

For the synthesis of proton-conducting materials, acrylic monomers (acrylonitrile, AN, and acrylic acid, AA), including monomers containing a sulfonic acid group (3-sulfopropyl acrylate potassium salt – SPAK), were used. The presence of the sulfo group provides proton-conductive properties of the material, since sulfo groups are strong proton donors in a humid environment. The choice of the functional monomer SPAK was due to its high level of proton conductivity.

The organic matrix was formed by UV-initiated polymerization. It was modified with silica nanodomains formed by the sol-gel process of alkoxysilanes. Two organosilicon precursors – tetraethoxysilane (TEOS) and 3-methacryloxypropyltrimethoxysilane (MAPTMS) – were used as starting materials for the sol-gel process. Feed compositions for organic/inorganic composites syntheses were as follows (wt %): AN – 40.0; AA – 20.0; SPAK – 25.0; EGDMA – 15.0; sol-gel system SG (TEOS or MAPTMS) – S1 - 0; S2 - 1.0; S3 - 3.0; S4 - 5.0; S5 – 7.0. Cross-linking agent ethylene glycol dimethacrylate EGDMA provides the formation of additional cross-links in the structure.

Sol-gel precursors were mixed with water and ethanol, stirred for 20 min at ambient temperature. H_3PO_4 was used as a catalyst. As a result of hydrolysis and polycondensation reactions that took place in the sol-gel system, the sol of silica nanoparticles was formed. Colloidal silica nanoparticles were added to the mixture of monomers before UV-irradiation.

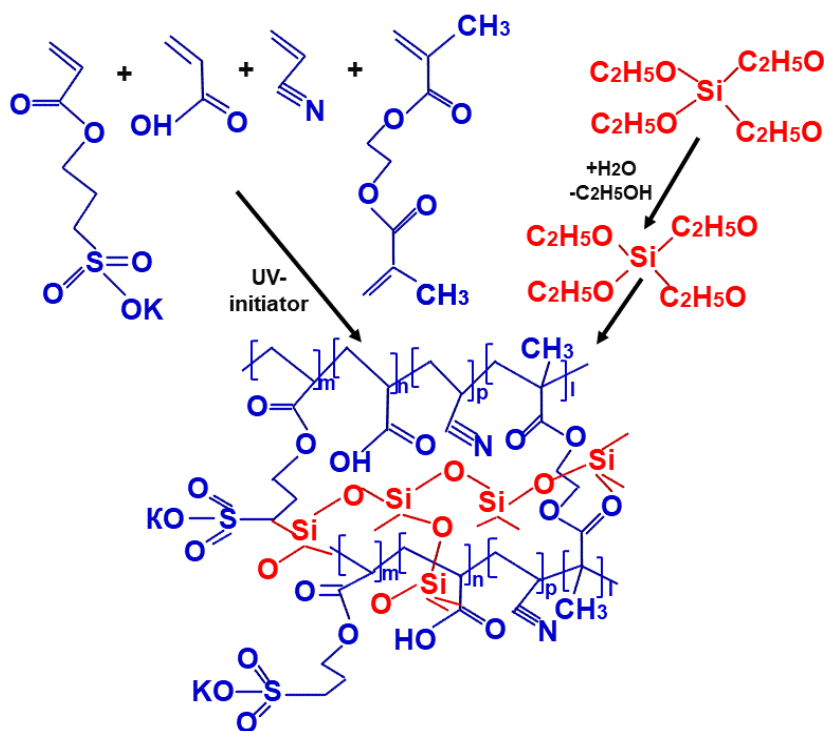


Fig. 1. Scheme of organic/inorganic composite synthesis.

The introduction of TEOS ensures the formation of a Si–O–Si network in the structure of the composite material (Fig. 1), as a result, a hybrid organic/inorganic network is formed in the copolymerization process. In this way, interpenetrating organic/inorganic networks with a specific structure provide channels for proton transport.

Since the sol-gel precursor MAPTMS, in addition to $-\text{SiOCH}_3$ groups, contains a reactive acrylic fragment that reacts with the double bonds of acrylic monomers being incorporated into the polymer chain, organic and inorganic blocks are strongly interconnected.

Therefore, the method we proposed involves UV polymerization of a mixture of acrylic monomers with the simultaneous *in situ* formation of a polymer/silica composite structure in which the organic and inorganic components are combined at the nanolevel.

SEM method established the formation of a dense uniform structure in the cross section, without cracks (Fig. 2a, 2b). The structure of the membranes prepared on the basis of MAPTMS was found to be more homogenous, evidencing the compatibilizing effect of MAPTMS on the nanocomposite structure.

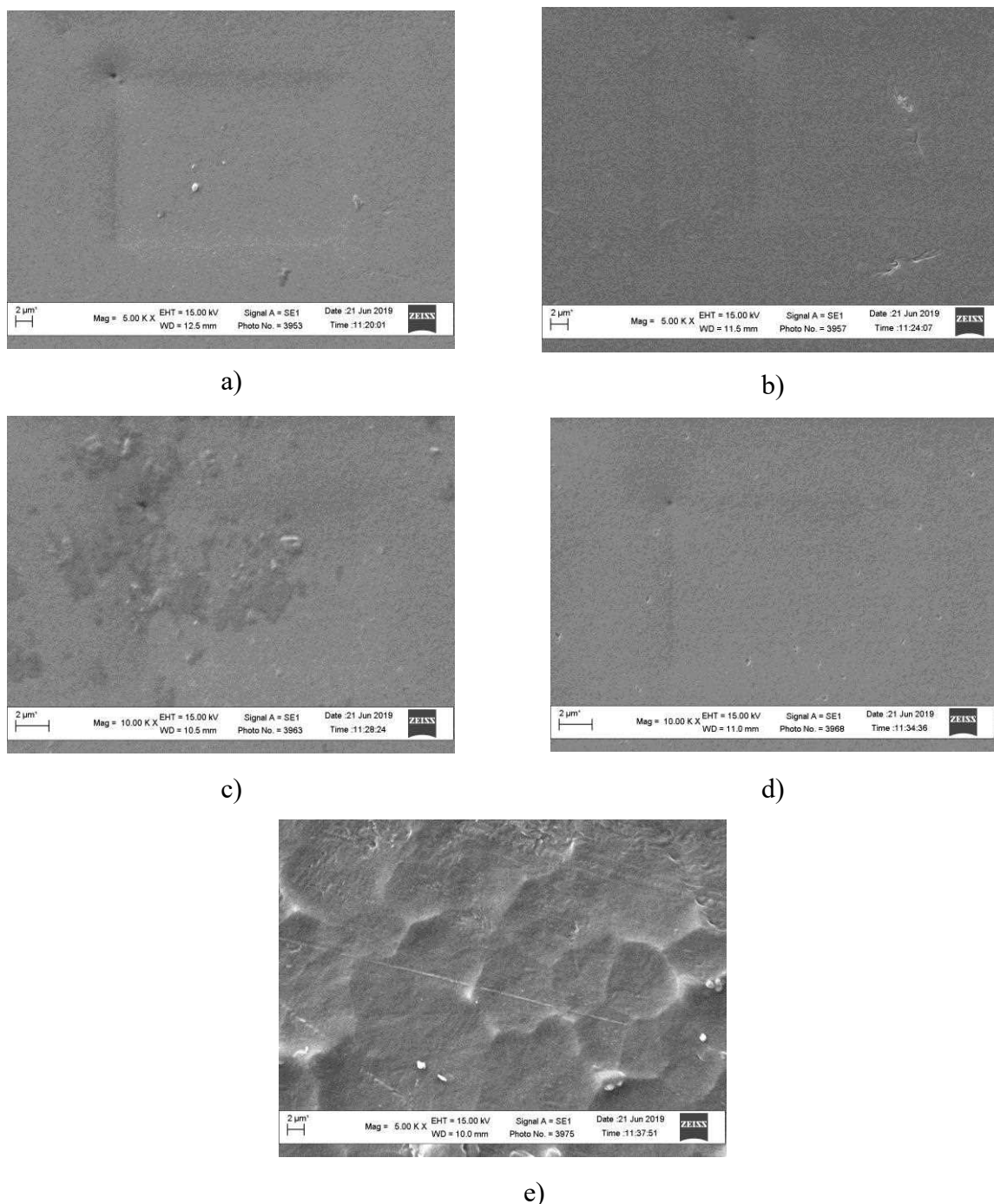


Fig. 2a SEM images of the membranes with TEOS-based sol-gel system:
a) S1; b) S2; c) S3; d) S4; e) S5.

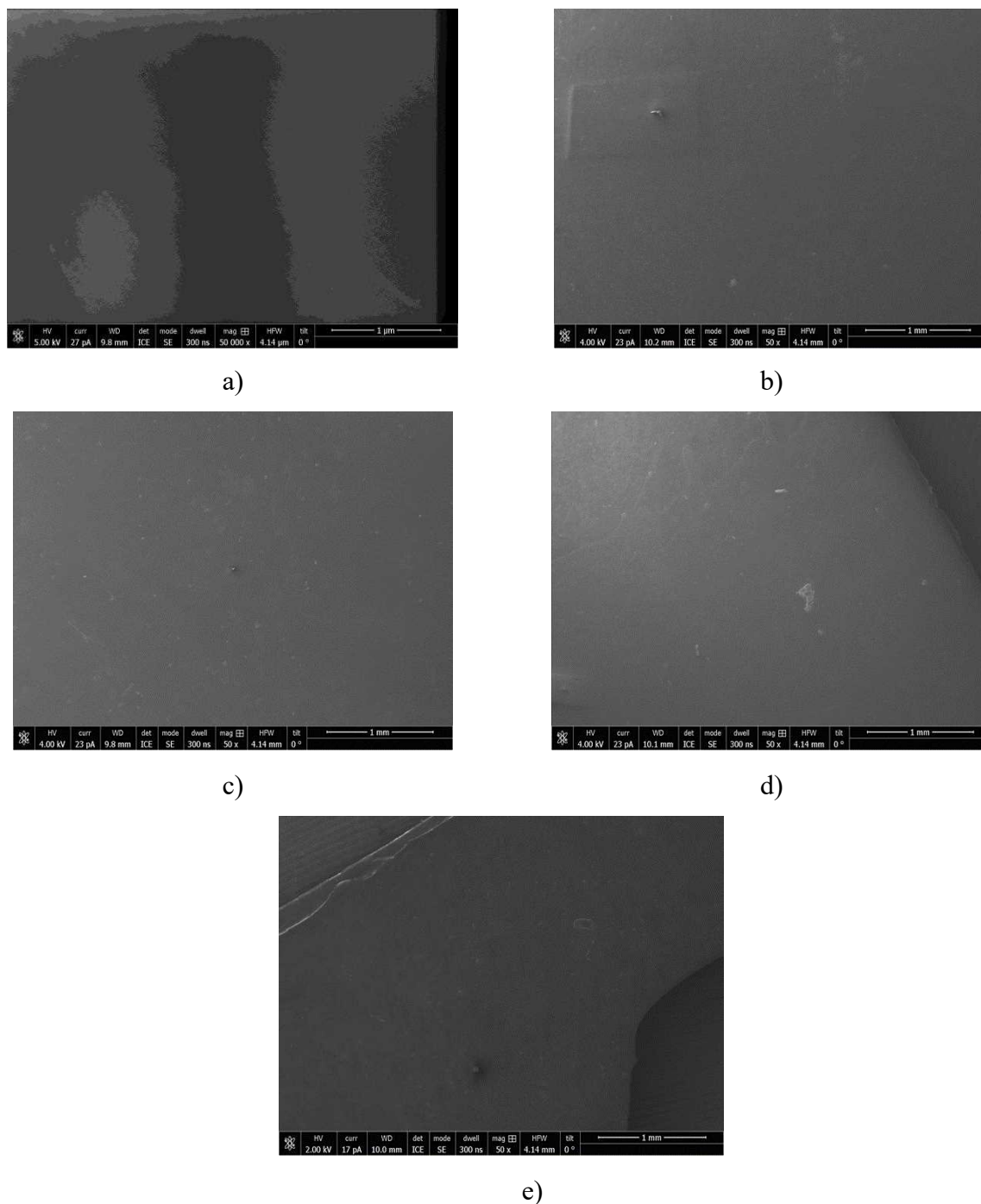


Fig. 2b. SEM images of the membranes with MAPTMS-based sol-gel system:
a) S1; b) S2; c) S3; d) S4; e) S5.

Water uptake is one of the most important properties of the membranes, as proton conductivity is correlated with its value. Modification of the nanocomposite membranes, as expected, contributes to better water retention, which may make the use of such membranes more effective in low-humidity conditions. The experimental results of the water uptake measurement are presented in Fig. 3 (water uptake vs content of the added precursor).

It should be noted that the water uptake value for the studied membranes prepared with the use of MAPTMS as a sol-gel precursor increases slightly (from ≈ 28 wt. % for S1 membrane to ≈ 32 wt. % for S3 membrane), and decreases slightly with increasing MAPTMS content, which correlates with the data of the wetting contact angle measurement and confirms the slight hydrophobicization of the material upon adding MAPTMS.

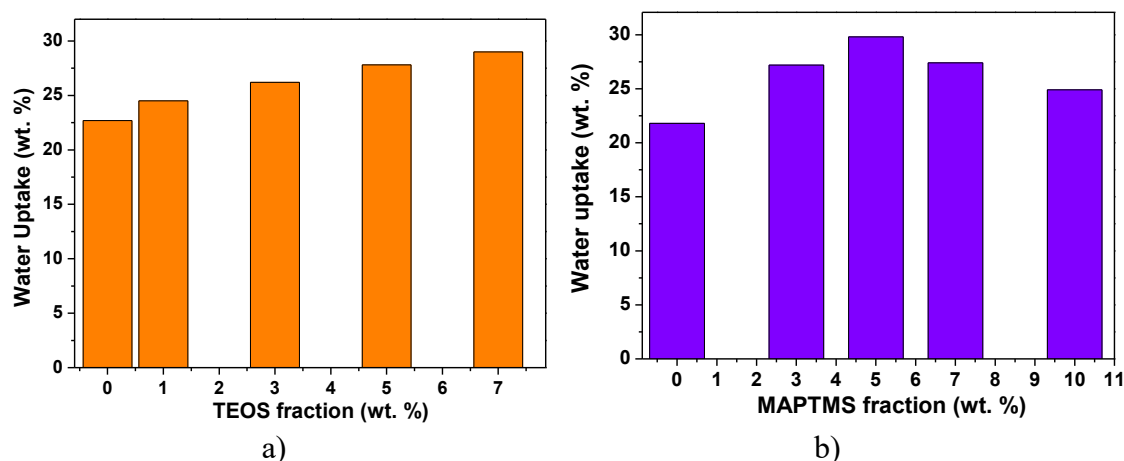


Fig. 3. Water uptake for S1 – S5 at the use of different precursors: a) TEOS; b) MAPTMS

Table 1

Proton conductivity of organic/inorganic materials at different temperatures (Sm/cm)

Sample	20°C	40°C	50°C	60°C
TEOS				
S1	$3.52 \cdot 10^{-3}$	$3.79 \cdot 10^{-3}$	$4.12 \cdot 10^{-3}$	$5.11 \cdot 10^{-3}$
S2	$7.31 \cdot 10^{-3}$	$8.93 \cdot 10^{-3}$	$9.14 \cdot 10^{-3}$	$1.02 \cdot 10^{-2}$
S3	$8.62 \cdot 10^{-3}$	$9.2 \cdot 10^{-3}$	$9.73 \cdot 10^{-3}$	$1.12 \cdot 10^{-2}$
S4	$7.14 \cdot 10^{-3}$	$8.62 \cdot 10^{-3}$	$8.98 \cdot 10^{-3}$	$9.94 \cdot 10^{-3}$
S5	$5.81 \cdot 10^{-3}$	$7.14 \cdot 10^{-3}$	$8.22 \cdot 10^{-3}$	$9.39 \cdot 10^{-3}$
MAPTMS				
S1	$0.88 \cdot 10^{-3}$	$1.50 \cdot 10^{-3}$	$2.31 \cdot 10^{-3}$	$2.98 \cdot 10^{-3}$
S2	$1.50 \cdot 10^{-3}$	$7.60 \cdot 10^{-3}$	$9.73 \cdot 10^{-3}$	$1.06 \cdot 10^{-2}$
S3	$6.30 \cdot 10^{-3}$	$9.80 \cdot 10^{-3}$	$1.02 \cdot 10^{-2}$	$1.16 \cdot 10^{-2}$
S4	$4.90 \cdot 10^{-3}$	$7.50 \cdot 10^{-3}$	$8.71 \cdot 10^{-3}$	$1.01 \cdot 10^{-2}$
S5	$3.80 \cdot 10^{-3}$	$5.20 \cdot 10^{-3}$	$7.62 \cdot 10^{-3}$	$9.38 \cdot 10^{-3}$

The values of proton conductivity for the synthesized membranes of two types (with the use of the different precursors of the sol-gel process) are high (Table 1); the maximum conductivity value reaches $1.16 \cdot 10^{-2}$ Sm/cm (sample S3 at a temperature of 60°C, sol-gel precursor MAPTMS), which is comparable to the proton conductivity of the Nafion117® membrane ($1.2 \cdot 10^{-2}$ Sm/cm). The high proton conductivity is due to self-organization processes that lead to the formation of a membrane matrix of hydrophobic polymer chains and clusters of hydrophilic functional groups that hold a large amount of water. As a result, a system of pores filled with an aqueous solution containing mobile ions was formed.

The obtained experimental results show that the proton conductivity of the membranes depends on their composition and temperature. For all samples, a symbiotic temperature-conductivity dependence is observed, which is evidence of the thermal activation nature of the proton transfer process in the studied temperature range. Adding an inorganic component to membranes increases the content of bound water in the membranes, which facilitates the ability to transport protons according to the Grothus mechanism by creating a continuous proton-conducting pathway.

Silica improves oxidative stability due to the cross-linking effect, which makes the membrane more compact.

As a result, the oxidative stability of silica/polymer membranes is somewhat higher compared to pure polymer membranes.

Conclusions

This study investigated the *in situ* synthesis of poly(AN-co-AA-SPAK-EGDMA)/SiO₂ proton conductive materials. To obtain organic/inorganic nanocomposites, we used the sol-gel process, since it is the most convenient procedure for incorporating an inorganic phase into an organic matrix under “mild” reaction conditions. The sol-gel process of the precursors TEOS and MAPTMS occurred in parallel with the UV-initiated polymerization of a mixture of acrylic monomers, resulting in the formation of a common silica/polymer network, which was additionally cross-linked by a structuring agent.

According to the classification of Sanchez K. et al. [6], the hybrids synthesized by us belong to class II of organic/inorganic materials, since there are covalent and hydrogen bonds between the inorganic and organic components, as well as effective packing of functionalized groups, which allows obtaining a homogeneous material. The homogeneous structure of the obtained materials was confirmed by SEM. The compatibilizing effect of MAPTMS on the nanocomposite structure was revealed.

Water uptake and proton conductivity were found to be high for both organic/inorganic membranes prepared using TEOS/MAPTMS sol-gel precursors. Proton conductivity of the membrane achieves $1.12 \cdot 10^{-2}$ Sm/cm in the case of the membranes prepared with the use of TEOS and $1.16 \cdot 10^{-2}$ Sm/cm in the case of the membranes prepared with the use of MAPTMS. The oxidative stability of proton-conducting silica/polymer membranes increased compared to polymer ones.

The synthesized membranes have the potential for application as proton-conducting membranes in fuel cells.

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Hydrothermal and Mechanochemical Modification as a Tool for Preparing ZrO₂ with Desired Physicochemical Characteristics and Improved Photocatalytic Properties

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Abstract. *Hydrothermal treatment of precipitated ZrO₂ at 300 °C promotes the transformation of amorphous ZrO₂ into a pure monoclinic phase, as well as the formation of a uniform mesoporous structure, which has higher thermal stability. Soft dry post-milling of monoclinic ZrO₂ causes the introduction of defects into its structure without a noticeable change in the porosity and preservation of the phase composition. The presence of defects is confirmed directly by UV-Vis spectra and indirectly by the manifestation of photocatalytic activity of milled samples under visible irradiation.*

Keywords: zirconium dioxide, hydrothermal treatment, milling, crystal and porous structure, photocatalysis.

Introduction

Zirconium dioxide is used as a catalyst or support material in the temperature range up to 900 °C. Monoclinic ZrO₂ is the only phase that is stable under these conditions. This is important because the use of metastable tetragonal and cubic ZrO₂ is accompanied by phase transformations and undesirable changes in structure during catalytic processes. Hydrothermal treatment (HTT) is the most effective low-temperature procedure for preparing ZrO₂, enabling the formation of a developed mesoporous and thermally stable structure. It is known that dry milling is an effective way of introducing oxygen vacancies OV_s into the structure of oxides, which can additionally enhance their catalytic activity.

Results and discussion

Initial ZrO₂ samples were prepared from zirconium oxynitrate aqueous solution using ammonium hydroxide as a precipitant at pH 7 and 9.5. The obtained ZrO₂ in the form of a wet gel and a dried xerogel was subsequently subjected to hydrothermal treatment (HTT) at 260-320 °C and equilibrium vapor pressure for 5-7 hours. Hydrothermally treated dried xerogels were subjected to mechanochemical treatment (MChT) in air (dry milling) at 300-500 rounds-per-minute (rpm) and ball-to-powder ratio (BPR) 10-25 for 30-60 min. A pure monoclinic phase with varying degrees of crystallinity (crystallite size is within 3-15 nm) is formed after HTT at 260-300 °C of ZrO₂ precipitated at pH 7 (Fig. 1). Full profile Rietveld refinement analysis confirms formation of almost pure, well-crystallized monoclinic ZrO₂ after HTT of wet gel and dried xerogel at 300°C.

Post-milling of the hydrothermally prepared monoclinic phase leads to the introduction of micro-strains into the crystal structure while maintaining the phase composition.

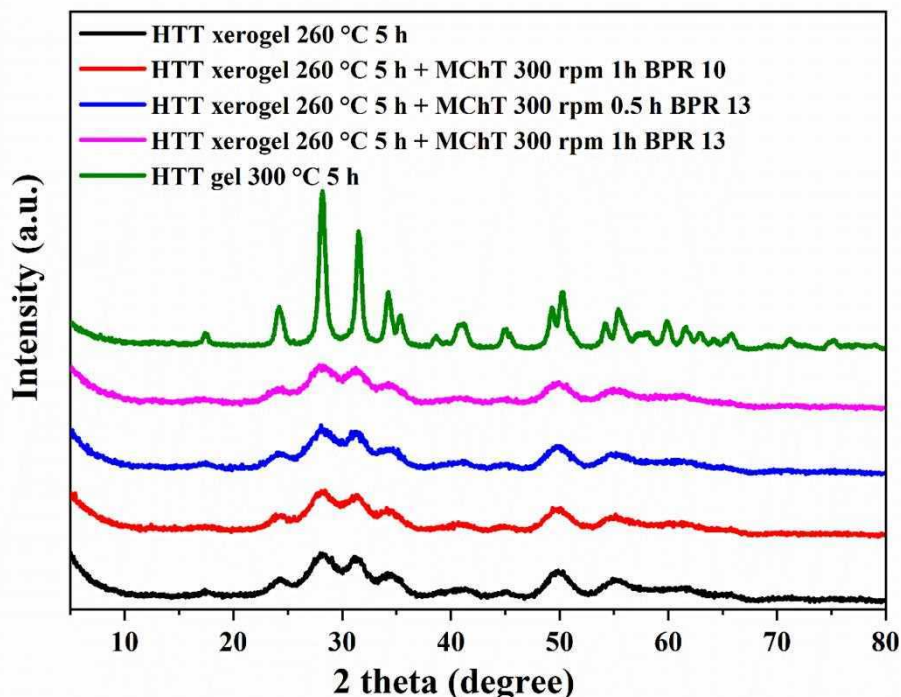


Fig. 1. XRD patterns for ZrO_2 , precipitated at pH 7, after HTT additional MChT under different synthetic conditions.

Nitrogen adsorption-desorption isotherms demonstrate the transformation of the micro-mesoporous structure of the initial precipitated ZrO_2 into a developed and uniform mesoporous structure with high specific surface area S , mesopore volume V_{me} and mesopore size d_{me} after HTT. This structure is largely preserved after post-milling. Moreover, the hydrothermal and post-milled samples have increased thermal stability of the porous structure compared to the initial precipitated sample (Table 1).

Table 1

Characteristics of porous structure for samples precipitated at pH 7

Conditions of modification	S , m^2/g	V_{me} , cm^3/g	d_{me}^* , nm
Initial pH 7	130	0.07	2.8
+ HTT xerogel 260 C	184	0.18	3.7
HTT xerogel 260 C + MChT 300 rpm 1h BPR 10	149	0.215	3.7
HTT xerogel 260 C + MChT 300 rpm 1h BPR 13	139	0.20	3.7
Initial pH 7	130	0.07	2.8
Initial + TT 500 C	27	0.07	6.5
HTT gel 300 C 5 h	60	0.17	9.7
HTT gel 300 C 5h + TT 500 C	61	0.24	9.7
HTT gel 300 C 7 h	48	0.18	9.7
HTT gel 300 C 7h + TT 500 C	44	0.17	9.7
HTT gel 300 C 7 h + MChT 500 rpm 0.5h	28	0.07	3.8; 13.0
HTT gel 300 C 7 h + MChT 500 rpm 0.5h+TT 500	28	0.07	3.8; 13.0
HTT xerogel 300 C 7 h	66	0.19	7.8
HTT xerogel 300 C 7 h + MChT 400 rpm	68	0.14	6.6
HTT xerogel 300 C 7 h + MChT 450 rpm	72	0.17	5.8
HTT xerogel 300 C 7 h + MChT 500 rpm	52	0.11	3.6; 32

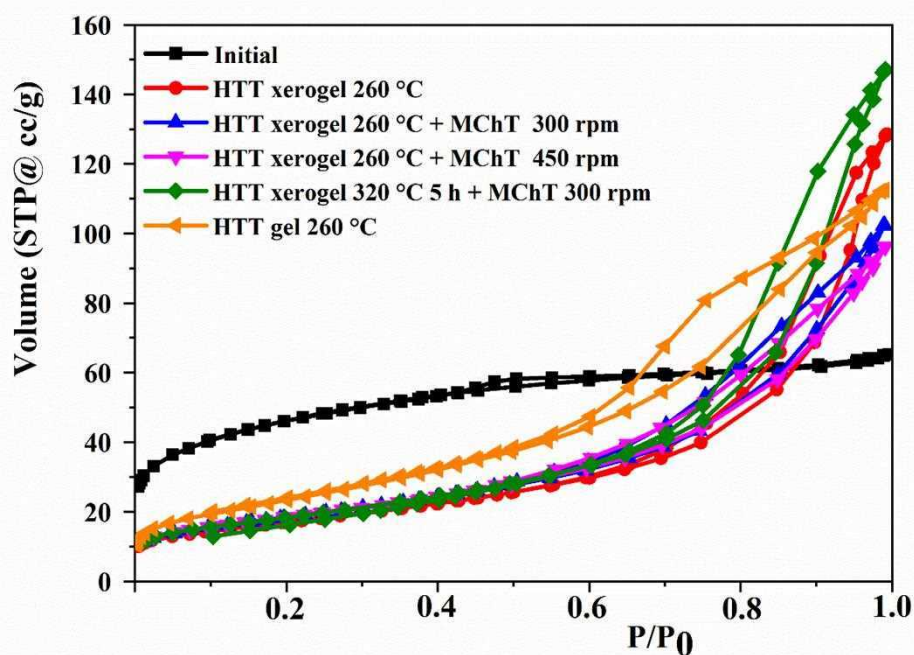


Fig. 2. Nitrogen adsorption-desorption isotherms for selected hydrothermal and post-milled samples

In general, zirconium dioxide is a semiconductor with a band gap of 5.1 eV, and it does not change during HTT. Post-milling results in a shift of absorption edge toward the visible region and corresponding narrowing band gap to 5.0 eV as well as the appearance of Urbach tail in the UV-Vis spectra of milled samples, which may be caused by the formation of OV's (Fig. 3). As a result of the extended absorption range to visible region, the second absorption edge is recorded in spectrum of milled sample, which corresponds to band gap at about 2.80 eV. It is important that post-calcination of these milled samples at 500 °C practically does not lead to a change in the spectra (Fig. 3). This is consistent with the thermal stability of the crystal structure of the milled samples, as indicated above.

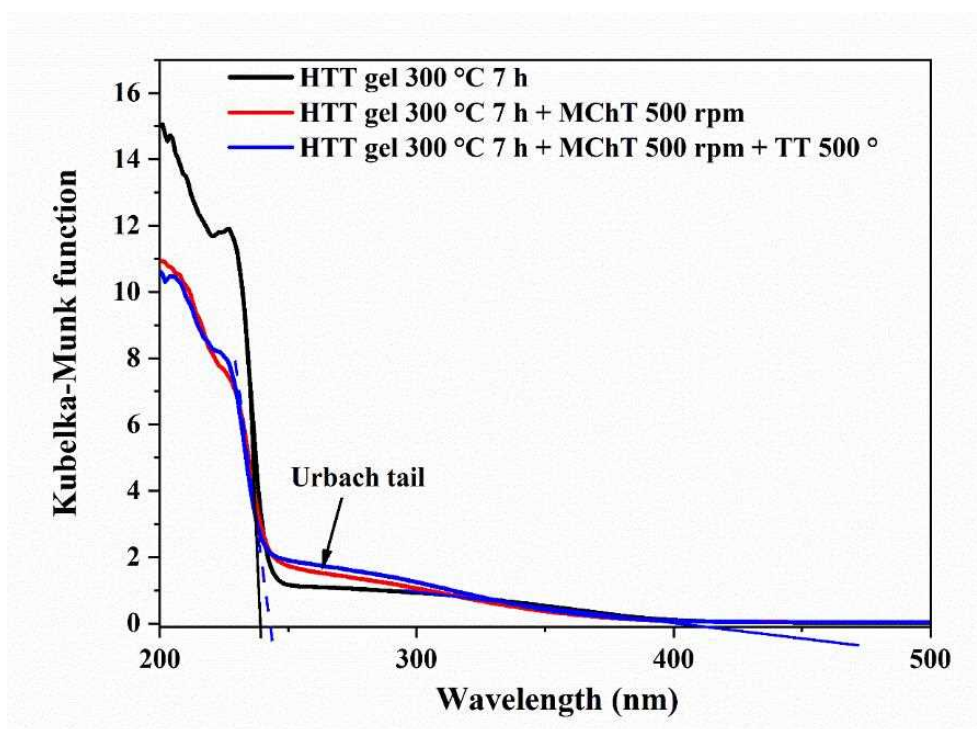


Fig. 3. UV-Vis spectra of samples after HTT, post-milling and calcination.

Due to its wide band gap, as-precipitated and hydrothermally modified zirconium dioxide is photocatalytically active only under the influence of UV radiation, while milling a hydrothermal sample causes it to acquire photocatalytic activity under visible light. This is confirmed by the results of photocatalytic degradation of dyes, safranin T, and Rhodamine B, in an aqueous medium.

Thus, the degree of discoloration of their solutions is 50-70% in 5 hours under the influence of visible light in the presence of milled ZrO_2 , and the degree of mineralization, the transformation of organic substances into less harmful inorganic ones, is 30-50%. Extra-modification of monoclinic ZrO_2 by mechanochemical introduction of Ni into its structure promotes the formation of a *p-n* heterojunction transition at the NiO/ZrO_2 interface, further improving the photocatalytic activity of the prepared compositions. As a result, their photocatalytic performance increases several times.

Conclusions

A new route for preparing a thermally stable mesoporous monoclinic ZrO_2 support with possible increased thermal stability, containing stable defects introduced by milling, is proposed. It uses the combined effect and advantages of both hydrothermal and mechanochemical methods. Particularly, ZrO_2 becomes active under visible light due to the introduced defects.

Acknowledgments

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Crystallization Parameters of CsPbBrCl₂ Melt

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Abstract. *Differential thermal analysis (DTA) was used to study the crystallization parameters of CsPbBrCl₂ perovskite. CsPbBrCl₂ melts and crystallizes in the temperature range of 510 – 570°C, depending on its dwell temperature. In the dwell temperature range of 574 – 625°C the crystallization of the melt is stabilized at a temperature of 560 ± 5°C.*

Keywords: DTA, Metal halide CsPbX₃ perovskites, crystallization.

Introduction

Metal halide CsPbX₃ (X = Cl, Br, I) perovskites are extremely interesting and promising semiconductor materials that have gained significant attention in recent years due to their exceptional optical and electronic properties [1-3]. These perovskites open up new opportunities for the production of highly efficient optoelectronic devices [4-6]. As thermal degradation becomes the main obstacle for industrial applications of all-inorganic cesium lead halide (CsPbX₃, X = Cl, Br, I) perovskite optoelectronic devices [7], therefore, the study of the thermal properties of such materials is very relevant. Differential thermal analysis is excellent for this purpose, providing information on thermal transformations and stability of materials, which is important for understanding their structure and properties. Knowledge of thermal characteristics will allow optimizing the growth of single crystals of these materials.

Experimental

The method of preparing ampoules and DTA processing of the thermograms was similar to the method described in detail in our previous work [8]. The samples were synthesized directly in the DTA ampoule in a total amount of 500 mg by melting of an equimolar amount of CsBr and PbCl₂ (ampoule 1 – A1) and CsCl, PbBr₂, PbCl₂ in a molar ratio of 1:0.5:0.5 (ampoule 2 – A2). The purity of the binary salts was at least 99%. The ampoules were evacuated using a vacuum pump up to $4.6 \cdot 10^{-2}$ Pa and sealed under the vacuum. DTA thermography includes several conditions:

- Thermocycling was carried out in the range of 300 – 660°C;
- Samples were heated to a certain temperature in the range of 550 – 660°C;
- The heating rates were 2 °C/min and 5 °C/min; dwell time – 30 min.

Results and discussion

The thermograms, which were obtained as a result of DTA, are graphical representations of thermal changes in the CsPbBrCl₂ melt during its heating and cooling. Fig. 1 represents such thermograms for CsPbBrCl₂ (A1) at $V_{h/c} = 5^\circ\text{C/min}$ and dwell time -30 minutes. From Fig. 1a, we see a highly overheated melt ($T_{\text{dwell}} = 647^\circ\text{C}$). In this case, the sample has completely melted even before the dwell starts, and crystallization occurs rapidly, since there is a needle-like effect (rapid

release of energy during the exothermic process). Usually, at such high dwell temperatures, there is a high rate of crystallization, which occurs with supercooling, because the temperature of the beginning of the crystallization effect (509°C) is clearly lower than the temperature of the beginning of the melting effect (548°C).

Gradually, in the following cycles, we lowered the dwell temperature. Thus, for example, at 615°C and 560°C (Figs. 1b and 1c) there is no so rapid crystallization effect. Since the lower the dwell temperature, the crystallization effect will be smaller and a little wider, so the crystallization process itself is not so fast. Already at relatively very low temperatures (553°C), it is clear that a small part of the sample has melted, and in fact,, only that small volume of liquid crystallizes on those fragments of the solid phase that remained in the melt (Fig. 1d).

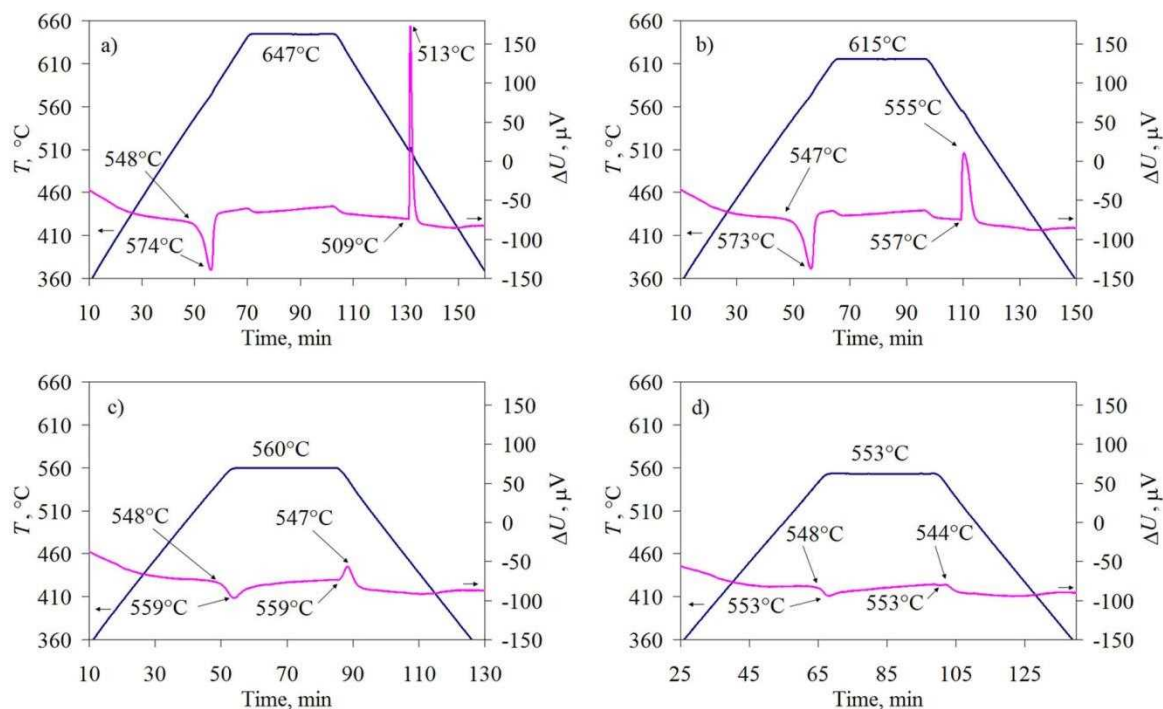


Fig. 1. Typical thermograms of melting and crystallization of CsPbBrCl₂ in dynamic thermal cycling conditions ($V_{h/c} = 5^{\circ}\text{C}/\text{min}$, dwell time – 30 min, A1).

The obtained experimental results showed that there is no significant difference between the crystallization parameters of the melts of ampoules A1 and A2. Fig. 2 shows the dependence of the record area of the crystallization effect of the CsPbBrCl₂ melt on the dwell temperature. For convenience, we have divided our graph into 3 conditional parts. In the first part, it can be seen that the sample is in a semi-liquid state (the temperature range of 550 -574°C). We can conclude that as the temperature increases in this interval, the proportion of the liquid phase increases, which then crystallizes and gives us a certain area of the crystallization record. In this part of the graph, with an increase in the dwell temperature, the area of the crystallization record increases from 0 to 88 a.u.

In Part II, where the dwell temperatures are 574-625°C, the recording area of the crystallization effect reaches a certain value and ranges between 88-100 a.u. We can assume that the sample is completely melted; however, with a temperature increase, the recording area of the crystallization effect also increases slightly. It is obvious that there are still some small fragments that have not melted. Most likely, these can be so-called clusters and can exist in a sufficiently wide temperature range.

Already when we overheat more than 625°C (part III), these clusters are completely destroyed and the melt is completely in a liquid state. Accordingly, the recording area of the crystallization effect increases slightly, and its values range from 92 to 107 a.u.

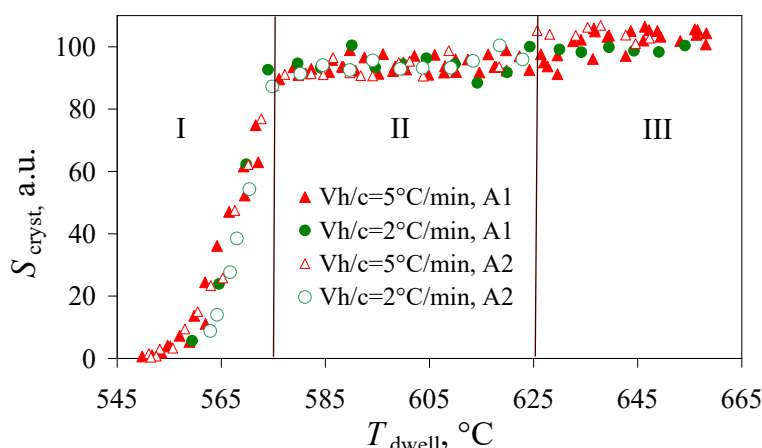


Fig. 2. Dependence of the record area of the crystallization effect of the CsPbBrCl₂ melt on the dwell temperature of the melt.

These same data are confirmed by the graph of the dependence of the crystallization temperature on the dwell temperature (Fig. 3). For convenience, we will divide this graph into 3 parts, which correspond to the other three parts in Fig. 2. It can be seen from Part I that the temperature of crystallization practically corresponds to the dwell temperature. This means that the sample crystallizes immediately after turning on the cooling process, that is, the so-called hot crystallization occurs. Such a phenomenon occurs in our sample during dwell at 550 - 574°C.

In the next part II, the crystallization temperatures reach a certain value, such as 560 ± 5°C. That is, in this temperature range, crystallization occurs without supercooling and more or less at a stable temperature. As already mentioned above, most likely small fragments (stable clusters) are present in the melt, which can serve as the center of crystallization and cause more or less uniform crystallization temperatures.

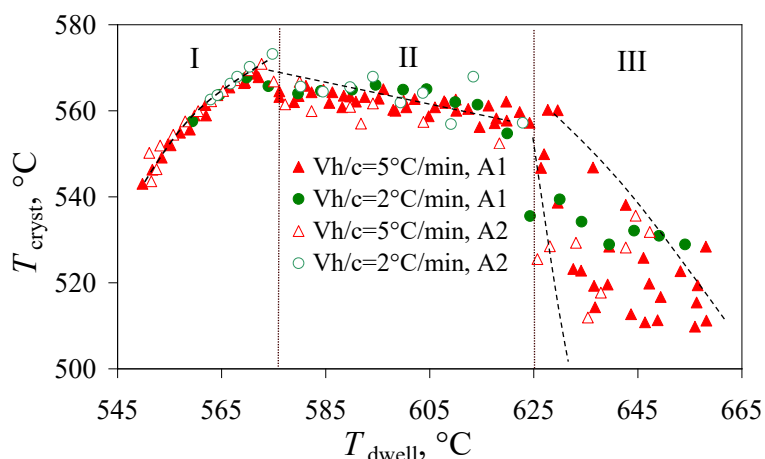


Fig. 3. Dependence of the temperature of the crystallization effect of the CsPbBrCl₂ melt on the dwell temperature of the melt.

At a dwell temperature above 625 °C (part III), these stable clusters begin to collapse; accordingly, there are no more particles in the melt that would be centers of crystallization. This causes the melt to begin to crystallize with supercooling. That is, the temperature of the beginning of crystallization is much lower than the temperature of the beginning of melting.

We also managed to display the kinetics of the crystallization process using the Arrhenius equation, namely its logarithmic form. Fig. 4 shows the dependence of the logarithm of the crystallization rate of the CsPbBrCl₂ melt on the inverse temperature. Based on the angle of slope of the straight lines, which are responsible for each certain interval of dwell temperatures, it is possible to draw a conclusion about the kinetics of the crystallization process. But for the reliability of the facts, we calculated the activation energies of the crystallization process for each part of the graph. It is this value that shows how easily the exothermic effect takes place.

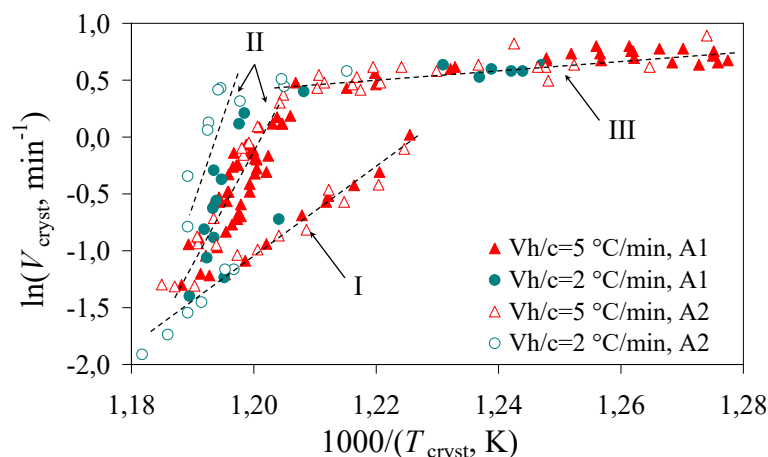


Fig. 4. Dependence of the logarithm of the crystallization rate of the CsPbCl₂Br melt on the inverse temperature.

The above data for describing the kinetics of the process are given in Table 1. From the equation of the straight line of the first part (I), which is responsible for the range of dwell temperatures of 550 – 574°C, we see that the activation energy of the crystallization process is quite large (320 kJ/mol). This means that it is difficult for the melt to crystallize, despite of the fragments of the solid phase that are present in the melt. Obviously, these fragments have composition and/or structure different from that of the melt.

Table 1

Calculated values of activation energy for the CsPbCl₂Br melt's crystallization process at different dwell temperatures

Dwell temperature, °C	The equation of a straight line	Activation energy, kJ/mol
550 - 574 (I)	$\ln V_{\text{cryst}} = 38498/T_{\text{cryst}} - 47.2$ ($R^2 = 0.96$)	320
574 - 625 (II), $V_{h/c} = 2^\circ\text{C/min}$	$\ln V_{\text{cryst}} = 94297/T_{\text{cryst}} - 112.7$ ($R^2 = 0.36$)	784
574 - 625 (II), $V_{h/c} = 5^\circ\text{C/min}$	$\ln V_{\text{cryst}} = 82637/T_{\text{cryst}} - 99.4$ ($R^2 = 0.83$)	687
>625 (III)	$\ln V_{\text{cryst}} = 4146/T_{\text{cryst}} - 4.5$ ($R^2 = 0.62$)	34

From the second part (II), which is responsible for the dwell temperature range of 574 – 625°C, we can see how the activation energy of the crystallization process has increased dramatically (784 kJ/mol for $V_{h/c} = 2^\circ\text{C/min}$ and 687 kJ/mol for $V_{h/c} = 5^\circ\text{C/min}$). The reason for this is the presence of clusters which, obviously, differ from the solid state structure with the strongest bonds. These clusters are stable in a wide temperature range and cause inhomogeneity of the melt and high activation energy of the crystallization process. When dwell temperatures are above 625°C (part III), the clusters break and the melt becomes homogeneous. Such melts crystallize quickly with supercooling and low activation energy (34 kJ/mol).

Conclusions

The parameters of CsPbBrCl₂ melt crystallization depend on the maximum temperature to which the sample was heated and held. CsPbCl₂Br melts non-isothermally, and in the temperature range of 550 – 574°C, the alloy is in a two-phase state: solid phase – melt. At these dwell temperatures, the melt crystallizes without supercooling, and the crystallization temperature exceeds the temperature at which CsPbBrCl₂ starts to melt. In the temperature range of 574 – 625°C the crystallization of the melt is stabilized at a temperature of 560 ± 5°C and the activation energy of the crystallization process is high due to the presence of stable clusters in the melt. At dwell temperatures above 625 °C, the crystallization of the CsPbBrCl₂ melt occurs with supercooling, and the crystallization process runs fast due to low activation energy.

Acknowledgments

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Effect of Chemical Etching on Photoinduced Modulation of Subterahertz Radiation by Crystalline Germanium

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Abstract. *The influence of the etching duration on the surface of Ge samples with different thicknesses (0.5, 1.6, and 2.3 mm) on their photomodulation of terahertz radiation with a frequency of $f = 130$ GHz was investigated. It was shown that pulsed lamp illumination of Ge samples with a thickness of 0.5 mm, chemically etched in a solution of 95 cm³ of 1% KOH and 75 cm³ of 60% H₂O₂ for different durations (3 and 42 min), leads to changes in the transmission of electromagnetic radiation: a decrease after 3 min and an increase after 42 min. In contrast, the etching of Ge samples with thicknesses of 1.6 mm and 2.3 mm results in a decrease in their electromagnetic radiation transmission upon illumination.*

Keywords: germanium, surface etching, terahertz radiation.

Introduction

Waves in the terahertz (THz) and sub-THz frequency ranges have potential applications in defense, telecommunications and radio engineering, medicine, and scientific research [1, 2]. This has led to a demand for devices that could effectively control these waves. A review of methods for modulating THz and sub-THz waves, including all-optical, electronic, and thermal, is presented in [3-5]. Optical modulators, the modulation of THz waves of which is carried out using a visible light source, are attractive due to their relative simplicity. Spatial modulation of THz radiation occurs by optically excited non-equilibrium carriers in photoconductive materials. In such materials, incident optical radiation with an energy exceeding the band gap generates charge carriers. This increases the conductivity of the irradiated material, making it opaque to sub-THz and THz radiation. Semiconductor materials are widely used in optical modulators of THz radiation. Silicon-based optical modulators are widely studied, due to the abundance of silicon and its low cost [4-5]. For silicon with a high resistivity, the change in conductivity when its surface is illuminated by optical radiation is relatively low. Achieving significant modulation of THz radiation requires high optical intensities. In [5], it was shown that using passivation of silicon wafers, their photosensitivity can be increased by many orders of magnitude with illumination. However, passivated silicon wafers have a long minority carrier lifetime equal to tens of milliseconds. The increased minority carrier lifetime leads to an increase in the switching time of optical modulators in the THz frequency range. Therefore, it is relevant to study semiconductor materials that have high sensitivity to optical radiation and a low minority carrier lifetime. In [6],

the effect of optical radiation on the propagation of THz radiation through single crystals of Si, Ge, and GaAs was theoretically studied. It has been shown that Ge wafers are an order of magnitude more sensitive than semiconductor Si with a minority carrier lifetime of ~ 1 ms, while GaAs has a minority carrier lifetime of ~ 1 ns, but requires significant optical illumination power densities of $\sim 10^4$ W/cm². Therefore, it is relevant to study the change in the photomodulation properties of Ge for the sub-THz and THz frequency range. As a result of mechanical and chemical treatment of germanium, its surface has a significant number of structural defects, both at the macroscopic and atomic levels. Since the state of the Ge surface significantly affects its photoconductivity [7], and therefore the transmission of sub-THz radiation, we investigated the effect of Ge surface treatment on the change in its photomodulation properties [8-10].

Experimental part

We studied the effect of the duration of Ge surface etching on its photomodulation of terahertz radiation with a frequency of $f=130$ GHz. Single-crystal Ge samples with a diameter of $d=30$ mm and thicknesses of $h=0.5$ mm, $h=1.6$ mm, and $h=2.3$ mm were used. The specific resistivity of Ge was 60.5 Ohm·cm. The surfaces of the Ge samples were mechanically processed: ground and polished. Chemical etching of the mechanically processed Ge samples was carried out in a solution of 95 cm³ of 1% KOH solution and 75 cm³ of 60% H₂O₂ solution at pH = 7...8. The etching process was controlled by changes in the thickness and mass of the samples. Control of changes in the sample thicknesses, depending on the etching time, was carried out using a Sloan Dektak IIA profilometer (Fig. 1a). For this purpose, a strip of photoresist grade FP-383 was applied to the Ge sample in the middle. The width of the photoresist strip was 4 mm. The photoresist was annealed for 45 minutes at a temperature of 120 °C. Before applying the photoresist, the surface of the Ge samples was degreased with acetone. Then the samples were etched for 3 and 42 minutes, respectively. After the etching process was completed, the photoresist was removed with a concentrated acetone solution. Using a profilometer, we observed the change in surface roughness at the interface protected by the photoresist and the etched surface (Fig. 1b). The etching rates were in good agreement with the results of work [11].



Fig. 1. The Sloan Dektak IIA profilometer (a) and the etching depth of the Ge sample surface at the interface of the photoresist-protected area and the surface etched for 42 min (b).

After the etching of single-crystal Ge samples, the photomodulation of sub-THz radiation by these samples was investigated. The stand used to measure the photomodulation of terahertz radiation is presented in Fig. 2.

Sub-THz radiation modulation was performed in pulse mode. For this purpose, the SOLIS-565D lamp radiation was modulated in the form of rectangular light pulses with a duration of 1 ms and an interval between pulses of 360 ms.

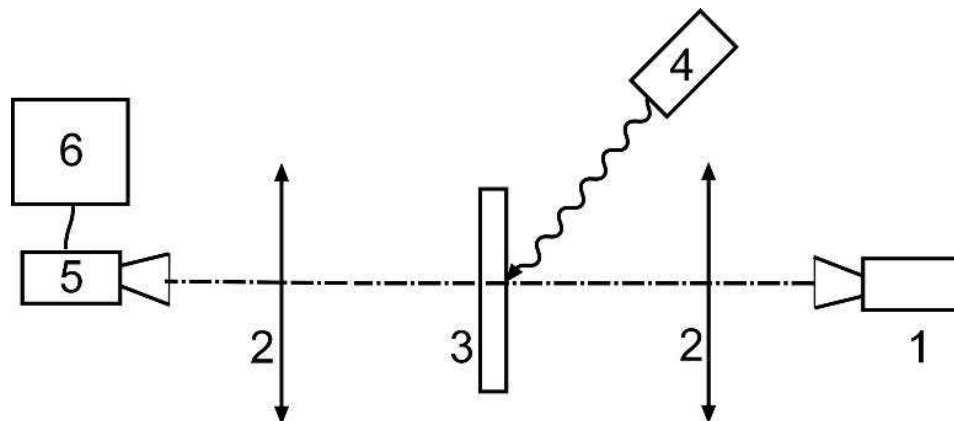


Fig. 2. Stand for studying photomodulation of sub-THz radiation at a frequency of $f=130$ GHz:

1 – transmitter with a horn antenna, 2 – Teflon lenses, 3 – photoconductive material, 4 – Thorlabs Solis – 565D lamp, 5 – receiver with a horn antenna, 6 – oscilloscope.

Results and Discussion

The results of pulse modulation of electromagnetic radiation with a frequency of $f=130$ GHz by Ge samples with different etching times and a thickness of $h=0.5$ mm are presented in Figs. 3 and 4.

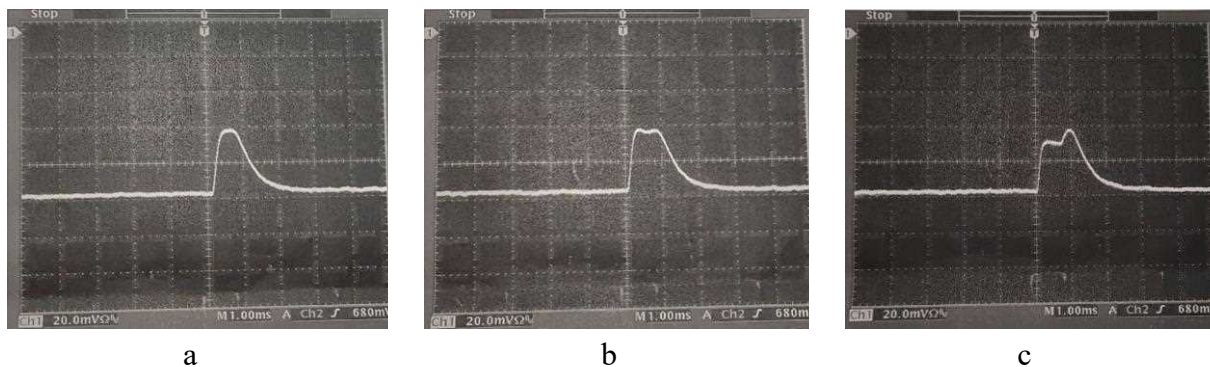


Fig. 3. Oscillograms of pulse modulation of electromagnetic radiation with a frequency of 130 GHz by a Ge sample, which was etched for 3 min, depending on the illumination intensity: 0.12 W/cm^2 (a), 0.33 W/cm^2 (b), 0.67 W/cm^2 (c).

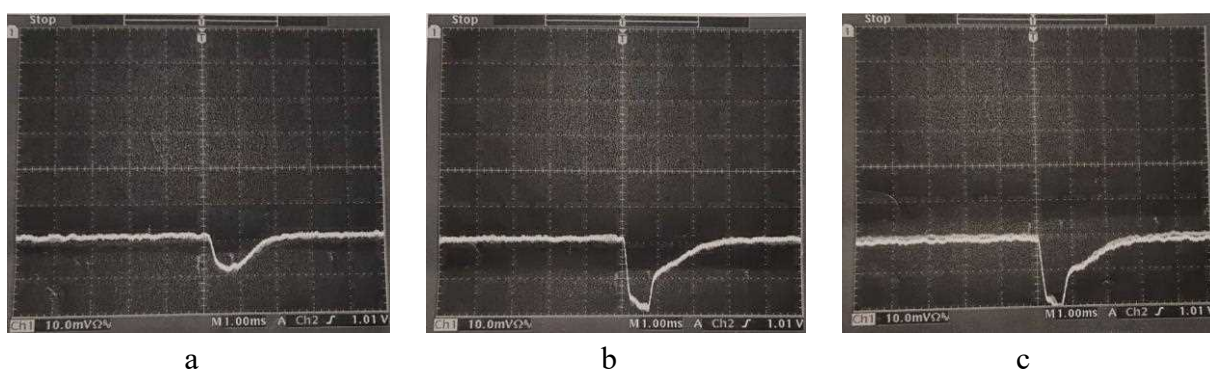


Fig. 4. Oscillograms of pulse modulation of electromagnetic radiation with a frequency of 130 GHz by a Ge sample, which was etched for 42 min, depending on the illumination intensity: 0.12 W/cm^2 (a), 0.33 W/cm^2 (b), 0.67 W/cm^2 (c).

In Figs. 3 and 4, the straight horizontal lines correspond to the transmission of electromagnetic radiation by a Ge sample without optical illumination. Pulsed lamp illumination of Ge samples chemically etched in a solution of 95 cm^3 of 1% KOH and 75 cm^3 of 60% H_2O_2 with different etching times, as can be seen from Figs. 3 and 4 lead to different effects of terahertz

radiation modulation. Thus, for Ge samples ($h = 0.5$ mm) etched for 3 minutes, the transmission decreases under pulsed lamp illumination as the illumination intensity increases. In contrast, for samples ($h = 0.5$ mm) etched for 42 minutes, the transmission increases as the illumination intensity rises.

Ge samples with thicknesses of $h = 1.6$ mm and $h = 2.3$ mm, when etched for both 3 min and 42 min, exhibited only a decrease in the transmission of electromagnetic THz radiation under pulsed lamp illumination. Such photomodulation properties of Ge of different thicknesses and different etching times can be explained by the fact that during chemical etching of Ge, a space charge region is formed [7]. At sample thicknesses $h \leq L_p$ (where L_p is the diffusion length) and large optical absorption coefficients α , which is characteristic of Ge, when illuminated by a Solis – 565D lamp, the volume has little effect on the processes of generation, recombination of carriers, as well as the diffusion-drift nature of their movement. In our case, $L_p = 2.5$ mm [6].

Conclusions

The photomodulation of sub-THz radiation by a single-crystal Ge sample with a thickness of 0.5 mm is strongly dependent on the etching time in a solution of 95 cm³ of 1% KOH and 75 cm³ of 60% H₂O₂ at pH=7...8. Depending on the etching duration, the transmission of sub-THz radiation through single-crystal Ge ($h = 0.5$ mm) can either decrease or increase. In contrast, for Ge samples with thicknesses of 1.6 mm and 2.3 mm, etched for 3 min and 42 min, the transmission of electromagnetic radiation under illumination decreased in all cases. To enhance the photomodulation characteristics of Ge for electromagnetic radiation, further investigation is required into the formation of porous Ge via chemical etching methods and its effect on photomodulation.

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Temperature Influence on the Rheological Properties of C9 Hydrocarbon Resin Solutions

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Abstract. *The study examines the behavior of C9 resin solutions synthesized via different oligomerization methods, focusing on dynamic viscosity, shear stress, and shear rate as functions of temperature. Viscosity decreases with rising temperature, confirming pseudoplastic behavior.*

Keywords: rheology, viscosity, shear rate, shear stress, C9 resin, solution.

Introduction

A primary method for producing gaseous olefins (ethylene and propylene) is the pyrolysis of petroleum feedstocks like gasoline and diesel. This process generates 30–35% liquid by-products, a complex mix of hydrocarbons, including dienes, olefins, and aromatics. Further processing yields light pyrolysis resin (pyrocondensate) with a boiling point up to 473 K, making up ~80% of liquid by-products. The C9 fraction (423–473 K), rich in unsaturated aromatics (~60 wt.%), serves as a raw material for hydrocarbon resins used in paints, coatings, adhesives, printing inks, and synthetic substitutes for vegetable oils and rosin [1, 2].

Oligomerization of the C9 fraction occurs via initiated or catalytic methods. Free-radical oligomerization, despite its industrial use, has drawbacks like high temperatures (453–493 K), long processing times, and high resin color index.

To reduce energy consumption and improve resin quality, a low-temperature (333–353 K) suspension and emulsion oligomerization method has been developed. Resins obtained by suspension oligomerization contain monomeric units of styrene and its derivatives. These products are characterized by a narrow molecular weight distribution and a lighter color. This technology reduces both the duration and energy consumption of the process compared to conventional methods [3].

Polymers and oligomers exhibit viscoelasticity, with viscosity influenced by temperature and pressure. Understanding resin viscosity under thermodynamic deformation aids in optimizing technical properties [4]. This study examines the temperature effect on the rheological properties of C9 hydrocarbon resin solutions obtained by different methods.

Experimental results and discussion

The dynamic viscosity of 10% resin solutions was measured using an Oswald viscometer with a 0.56 mm capillary. Flow time was recorded at six temperatures (293–343 K, in 10 K increments). The viscometer was placed in a constant-temperature water bath, and the solution was stabilized for 10 minutes before measurement. Flow time was measured with 0.1 s accuracy, with at least three measurements averaged for viscosity calculation.

The density of the resin solution and pure benzene was determined by the dilatometric method. Shear rate was calculated from the volumetric flow rate and capillary dimensions, while shear stress was derived from the pressure drop and capillary diameter [5].

The studied resins were obtained using different methods based on the C9 fraction of liquid by-products from diesel fuel pyrolysis. The synthesis method and properties of the resins are shown in Table 1.

Table 1

Production conditions and properties of hydrocarbon resin

Resin	Synthesis method	C9 resin structure	Molecular mass	Softening point, K
1	Initiated oligomerization (initiator: di- <i>tert</i> -butyl peroxide, reaction temperature - 473 K, reaction time - 6 hours.	Styrene-cyclopentadiene resin	670	356
2	Emulsion oligomerization (initiator: potassium persulfate, reaction temperature – 323 K, reaction time – 3 hours.	Styrene resin	690	358
3	Suspension oligomerization (initiator: benzoyl peroxide, added in 6 dosages, reaction temperature – 353 K, reaction time – 3 hours.		500	348
4	Initiated oligomerization of the C9 fraction after suspension oligomerization (initiator: isopropyl benzene hydroperoxide, reaction temperature – 453 K, reaction time – 6 hours.	Cyclopentadiene resin	650	354

The dynamic viscosity varies from 0.51 to 1.60 mPa·s (Fig. 1). The viscosity of the studied resins decreases with increasing temperature. These findings confirm the temperature dependence of viscosity, which is characteristic of pseudoplastic non-Newtonian fluids.

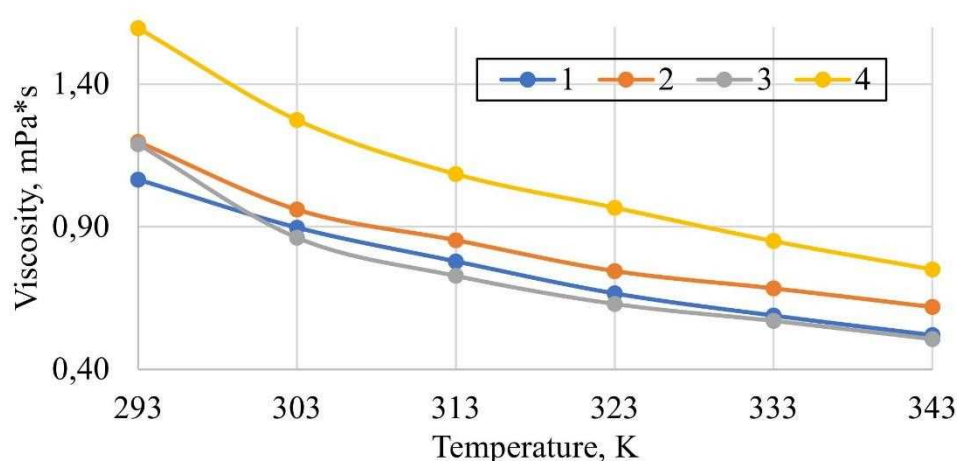


Fig. 1. Resin solution dynamic viscosity as a function of temperature.

The most significant changes in viscosity were observed in resin (1). At 293 K, resin (1) exhibits an initial viscosity of 1.07 mPa·s, which decreases to 0.52 mPa·s at 343 K. The difference in dynamic viscosity values for the resin solutions ranges from 0.93 to 0.98 mPa·s. The correlation between temperature and dynamic viscosity ranges from -0.95 to -0.99.

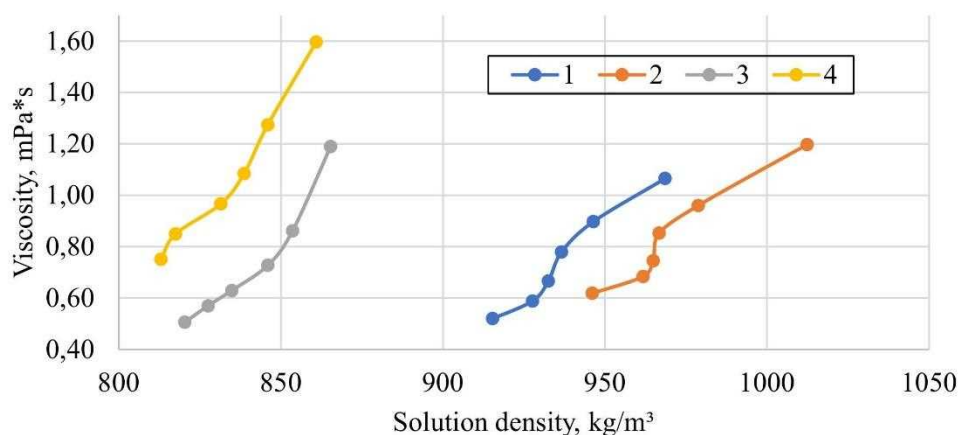


Fig. 2. Resin solution dynamic viscosity as a function of density.

The density of 10% resin solutions in benzene in the temperature range of 293–343 K varies from 1012.4 to 812.5 kg/m³ (Fig. 2). In the temperature range under consideration, the greatest variation in density was observed in the case of a resin solution of (2) – 66.3 kg/m³, while the lowest value was recorded for resin (4) – 32.9 kg/m³.

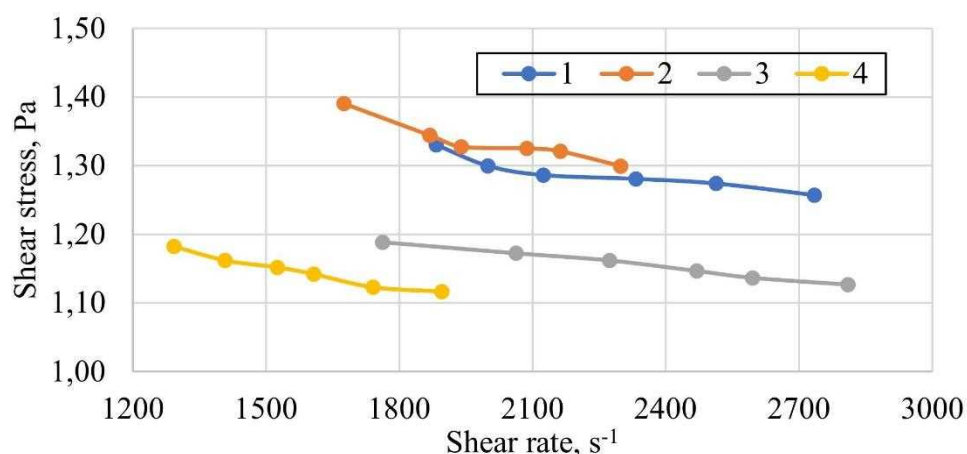


Fig. 3. Shear stress as a function of shear rate.

The shear rate vs. shear stress relationship (Fig. 3) was nonlinear for all samples, confirming their non-Newtonian behavior. The observed decrease in shear stress with increasing shear rate indicates shear thinning, a characteristic of pseudoplastic fluids. At high shear rates (>2000 s⁻¹), the shear stress values for all samples converge, suggesting reduced viscosity and more uniform flow behavior. Thus, all samples can be classified as pseudoplastic non-Newtonian fluids that undergo shear-induced liquefaction.

The temperature corresponding to the largest change in viscosity (critical temperature) is 303 K in all cases. The values of the temperature coefficient for the temperature range of 293–343 K are presented in Table 2.

Temperature significantly influences the rheological properties of the resins under consideration. The temperature coefficient, which quantifies the degree to which dynamic viscosity undergoes a change when the temperature is elevated or depressed by 1 K, exhibits negative values for all resins. This finding indicates a decline in viscosity with an increase in temperature from 293 K to 343 K. With increasing temperature, the density-to-viscosity ratio rose for all resins, reflecting the general viscosity decrease upon heating. Resin (4) showed the highest stability in this parameter, confirming its suitability for industrial applications requiring consistent rheological properties.

Table 2

The rheological properties of hydrocarbon resin solutions

Property	Resin 1	Resin 2	Resin 3	Resin 4
Temperature Coefficient (mPa·s/K)	−0.011	−0.012	−0.014	−0.017
Density per Unit Viscosity (293 K), (m ^{−1} ·s ^{−1})	909.1	845.4	727.6	539.3
Density per Unit Viscosity (343 K), (m ^{−1} ·s ^{−1})	1760.0	1529.1	1620.9	1083.7
Flow Index (n)	−0.129	−0.187	−0.110	−0.143
Consistency Constant (Pa·s ⁿ)	3.49	5.55	2.71	3.29

The flow index (n), which defines the shear stress dependence on shear rate, also varied with temperature. All tested resins had n values below 1, indicating pseudoplastic behavior. Cyclopentadiene resin (4), with significant viscosity changes under heating, emerged as a strong candidate for high-temperature paints and coatings. Meanwhile, styrene resin (2), demonstrating exceptional stability under high shear stress, is promising for applications involving heavy mechanical loads, such as rubber compounds and modified bitumen materials.

Conclusions

The dependence of the dynamic viscosity of hydrocarbon resin solutions on temperature, solution concentration, and synthesis method was studied. It was found that as the temperature increases, the rheological properties of the solutions approach those of non-Newtonian fluids, as confirmed by their pseudoplastic behavior. It was determined that the dynamic viscosity of resin solutions depends on both temperature and solution composition.

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We are grateful to the brave people of Ukraine.

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Studying the Rheological Behaviour of Polyamide Nanocomposites

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Abstract. *The composition and derivation conditions impact on the rheological behavior of polyamide nanocomposites were researched. The dependence of the nanocomposite flow curves on the channel length, flow velocity, channel geometry parameters, and the concentration of the modified filler was determined. It was found that modifying polyamide 6 has a positive effect on the rheological properties, making it possible to regulate the technological and operational characteristics.*

Keywords: volumetric flow rate, polyamide 6, montmorillonite-polyvinylpyrrolidone blend, flow curves, modification, pressure flow rate.

Introduction

In previous work [1], the montmorillonite was modified with polyvinylpyrrolidone in solution by the application of an ultrasonic field. The montmorillonite-polyvinylpyrrolidone blend (MPB), obtained in the form of a finely dispersed powder with a component ratio of 1:5 [2, 3], was used to prepare polyamide 6-based nanocomposites. Such composites possess quite unique properties, which are primarily caused by the complexity and peculiarity of the structure [4]. Polymers are characterized by a wide range of physical, mechanical, and rheological characteristics, which significantly depend on many factors, in particular: structural parameters, temperature, duration, and frequency or velocity of loading, pressure, type of tension, heat treatment, nature of the environment, etc. The type of changes is also influenced by flow rate, channel geometric parameters, nature of melt, etc. [5].

Therefore, studying the fluidity of polymers makes it possible to evaluate the suitability and processing conditions of polymers in a wide range of shear rates.

Purpose of the research

The aim of this work was the investigation of the rheological properties of modified polyamide 6-based nanocomposites in a wide range of parameter changes.

Materials and methods of research

The main materials used in the research were the following:

Polyamide PA6-210/310 with MFI_{230/2.16} = 19 g/10 min, melting point 488 K, density ρ_{20} = 1.12 g/cm³, relative viscosity 2.68, was used in the research. Prior to use, the PA-6 was vacuum dried at 363K for 2 hours.

The montmorillonite-polyvinylpyrrolidone blend (MPB), derived from a solution in the ultrasonic field [2, 3] with a ratio of MMT: PVP = 1:5, was used as a modifier for polyamide. The flow curves were taken according to ISO 1133-76 [6].

Research results and discussion

The flow curves (dependencies between shear stress τ and shear rate $\dot{\gamma}$) were recorded using the constant pressure viscometer at a constant temperature of 230 °C, but at different loads and capillary length to diameter ratios (l/d). To plot the flow curves, it was calculated [7, 8]:

– shear rate in the capillary (1):

$$\dot{\gamma}_i = \frac{4 \cdot Q_i}{\pi \cdot r^3} \quad \text{or} \quad \dot{\gamma}_i = \frac{4 \cdot r^2 \cdot h_i}{r^3}, \text{ s}^{-1} \quad (1)$$

where: r – capillary radius, m; Q_i – material flow rate, m³/s; h_i – piston descent speed determined for each load, m/s.

– shear stress (2):

$$\tau_i = (P_i - P_{ip}) \cdot \frac{r}{2 \cdot L_j} \quad (2)$$

where: L – capillary length; P_i – the piston pressure on material; P_{ip} (inlet pressure) – pressure required to ensure flow through the capillary with a length of L_i ; j – capillary index.

– effective viscosity (3):

$$\eta_{\text{eff}} = \frac{\tau}{\dot{\gamma}}, \quad (3)$$

On the basis of the data obtained, the graphs of the dependencies $\tau=f(\dot{\gamma})$ and $\eta=f(\dot{\gamma})$ were plotted in logarithmic coordinates.

The flow curve was divided into intervals. The n value, which is inversely proportional to the tangent of the angle of inclination to the curve, was determined for each interval. The calculated velocities were assigned the corresponding values of shear stress, on the basis of which the flow curves were constructed in true coordinates. The viscosity coefficient k was detected via extrapolation to the value $\tau=0$, with the further determination of the segment length, which is cut off on the ordinate axis.

The pressure created by the piston on the material is calculated as follows (4):

$$P_i = \frac{40 \cdot G_i}{\pi \cdot D^2}, \text{ (Pa)} \quad (4)$$

where: P – the piston pressure, n/m²; G – the mass of the load, kg; D – the diameter of the piston of the device, m (0.0095 m). Thereby, at a load the $G = 0.750 \text{ kg} \rightarrow P_1 = 0.11 \text{ MPa}$; $G = 2.16 \text{ kg} \rightarrow P_2 = 0.31 \text{ MPa}$; $G = 5.0 \text{ kg} \rightarrow P_3 = 0.71 \text{ MPa}$.

The next step was to determine the (Q) volumetric flow rate of the material for different l/d ratios. The volumetric flow rate was calculated using the formula (5):

$$Q = \frac{m}{t \cdot \rho}, \text{ (m}^3/\text{s)} \quad (5)$$

where: m is the mass of the flowing material (kg); t is the flow time (s); ρ is the material density under test (kg/m³). The calculated volumetric flow rates for different l/d ratios are given below in Table 1.

Table 1

Dependence of volumetric flow rate on load and l/d ratio
for PA-6 and its complex with MPB

Material	L/d ratio	$Q \cdot 10^{-2}, \text{ m}^3/\text{s}$		
		$G=0,750 \text{ кг}$	$G = 2,16 \text{ кг}$	$G = 5,0 \text{ кг}$
PA - 6	3.4	0.69	2.08	7.5
	9.2	0.2	0.89	2.3
PA-6+10% MPB	3.4	1.04	3.7	5.2
	9.2	0.48	0.33	3.5

On the basis of the calculated indicators, we draw a graph of the (Q) volumetric flow rate on the (P) pressure dependence for different l/d ratios.

Applying the obtained dependencies (Fig. 1), we select several values of Q: Q_1 , Q_2 , etc., and find the appropriate values of P: P_1 , P_2 , etc., in accordance with the Q flow rates and plot the $\Delta P = f(l/d)$ dependence (Fig. 2).

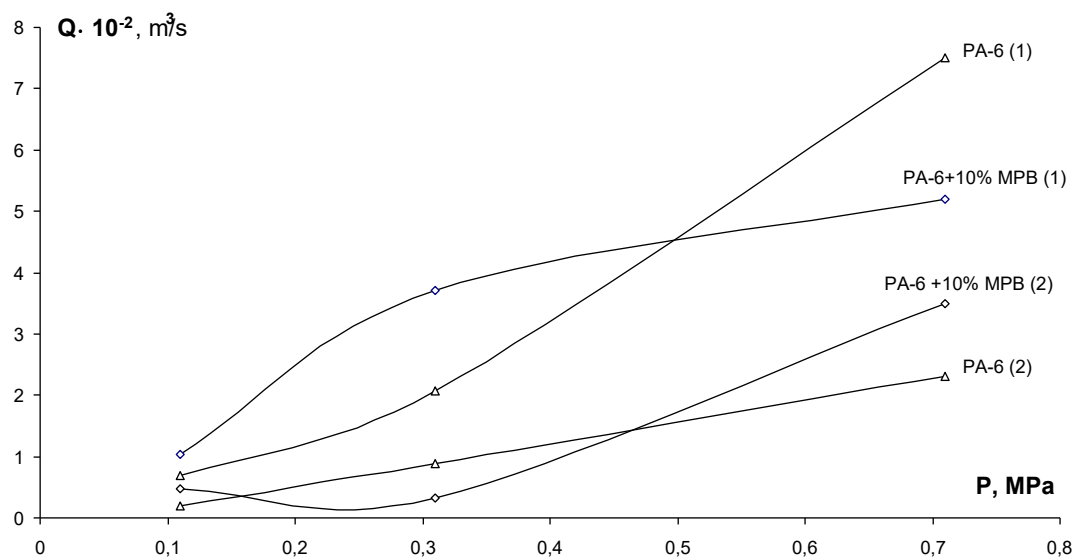


Fig. 1. Dependence of the volumetric flow rate of PA-6 and of its composition on the pressure at different l/d ratios: 1 – $l/d = 3.4$; 2 – $l/d = 9.2$.

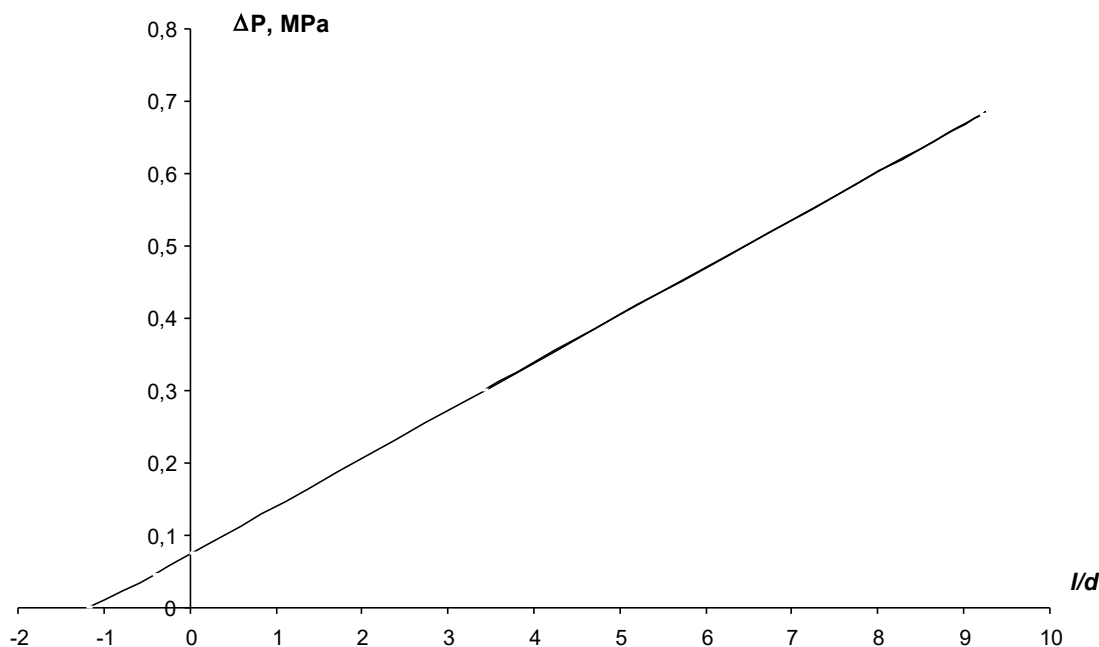


Fig. 2. Dependence of (ΔP) pressure loss on (l/d) ratio.

Extrapolating the obtained dependence to the pressure drop zero value, we obtain the inlet correction given in the relative lengths of the channel. Inlet correction $\nu = 1.2$.

For each selected value of Q, the shear stress τ , the shear rate $\dot{\gamma}$ in the capillary as well the effective viscosity η_{ef} are being calculated (Table 2).

Table 2

Shear stress, shear rate and effective viscosity of the compositions

$Q \cdot 10^{-2}, \text{m}^3/\text{s}$	τ, Pa	$\dot{\gamma}, \text{s}^{-1}$	$\eta_{ef}, \text{Pa}\cdot\text{s}$
1.2	0.028	0.013	2.15
2.5	0.033	0.027	1.22
3.5	0.034	0.038	1.26

As we can see, as the volume of material consumed increases, the shear stress and shear rate also increase, but not significantly. Simultaneously, the effective viscosity of the compositions decreases as the shear rate increases.

Conclusions

The conducted studies on the rheological behavior of polyamide composites made it possible to assess their suitability for processing in a wide range of shear rates.

It was established that the polyamide 6-based nanocomposite modified with a montmorillonite-polyvinylpyrrolidone mixture is characterized by the processability inherent in thermoplastics, which makes them promising materials for a wide range of applications, especially in industries where a combination of high-performance characteristics with production efficiency is required.

The results of these studies expand knowledge about the rheology of nanocomposites, contributing to the development of a new generation of materials with improved properties.

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Characterization of Miscanthus Biomass Waste -Derived Biochar Produced by Oxydative Pyrolysis: Implications for Carbon Sequestration

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Abstract. *This study explores biochar production from Miscanthus waste biomass via oxidative pyrolysis at 600°C. The resulting biochar shows high stability, enhanced moisture retention, and a significant calorific value. Its superior physicochemical properties, including high fixed carbon content and specific surface area, make it a promising material for soil and energy applications.*

Keywords: pelletized Miscanthus waste biomass, oxidative pyrolysis, biochar surface area, porosity.

Introduction

Biochar is a product of the pyrolysis of organic raw materials, mainly wastes, formed under conditions of absence of low oxygen availability [1]. The thermal treatment of biomass at temperatures between 300–750°C results in the formation of a high-carbon material with unique physicochemical properties. During pyrolysis, lignocellulosic components (cellulose, hemicellulose, and lignin) undergo processes of depolymerization, fragmentation, and cross-linking, which lead to the formation of products in various aggregate states: solid (biochar), liquid (biooil), and gaseous (biogas, i.e. CO₂, CO, H₂, hydrocarbons) [2].

Biochar is a highly stable material with an expected lifespan of thousands of years, distinguishing it from other soil amendments like compost and animal manure, which decompose much more rapidly [3]. Thanks to its porous structure, biochar has the ability to enhance carbon absorption in soil, which can contribute to the reduction of CO₂ emissions. Its addition to soil positively impacts water balance and improves nutrient retention, thereby increasing soil fertility [4].

One of the main advantages of biochar is the ability to stimulate microbial processes in soil. It promotes the growth of microorganisms that decompose organic matter and enhance nutrient availability for plants. Biochar influences the composition of microbial communities by altering the ratio of microorganisms and their functions [5,6].

The properties of biochar are influenced by various factors, with the most important being the type of feedstock, pyrolysis temperature, and process duration [7-9]. In Ukraine, biochar production is primarily focused on wood processing, while the use of plants' waste biomass, such as straw, corn stalks, and sunflower stems, is still in the early stages of development, mainly

limited by laboratory-level research. However, expanding biochar production from agricultural waste could become a significant part of the circular economy, helping to reduce waste and enhance the efficiency of land resource use.

A promising direction for biochar production can be the utilization of *Miscanthus* biomass during its first and second years of growth. At the early stages of cultivation of this crop, its yield is typically low, making the use of the first two years of vegetation biomass as an alternative energy economically invisible. However, rather than considering it as waste, this biomass can be effectively processed into biochar, a valuable product with added value. This approach not only promotes the rational use of resources but also ensures the sustainable development of the bioenergy sector.

The study aimed to analyze the quality of biochar produced from *Miscanthus* waste via pyrolysis, evaluating a number of physicochemical parameters of the material that determine its effectiveness during agricultural and ecological applications.

Materials and methods

Pelletized *Miscanthus* waste was carbonized using oxidative pyrolysis, which ensured limited oxygen access. The characteristics of the initial pelletized *Miscanthus* waste are presented in Table 1.

Table 1

Physicochemical characteristics of Pelletized *Miscanthus* waste

No	Parameter	Value
1	Pellet diameter	6–8 mm
2	Pellet length (max)	25–30 mm
3	Ash content on dry mass	$\leq 3\%$
4	Moisture content	$\leq 10\%$
5	Bulk density	640–670 kg/m ³
6	Calorific value	18.0–20.1 MJ/kg
7	Ash melting temperature	1180–1200 °C
8	Sulfur content	$\leq 0.02\%$
9	Volatile matter content	85–89%
10	Carbon content	~ 46%

The pyrolysis was conducted in a reactor with an open top and restricted air access entitled "Farmer.". The reactor was designed at the Institute for Renewable Energy Sources of the National Academy of Sciences of Ukraine, and the utilized technology was described in detail earlier [10].

The process was conducted with an initial weight of *Pelletized Miscanthus waste* in the reactor equal to 41.25 kg. The pyrolysis process yielded 9.10 kg of biochar, corresponding to a biochar yield of 22%. The reaction temperature was constantly maintained at 600°C, with a total pyrolysis duration of 240 minutes. The average energy demand for biochar production was calculated as 3.0 W/kg. The hot pyrolysis gas was burned in a flare to reduce environmental pollution from the harmful gases.

The physicochemical properties of the received *Miscanthus* biochar were evaluated based on specific surface area (m²/g), total pore volume (cm³/g), moisture content (%), volatile matter

content (%), fixed carbon content (%), ash content (%), and calorific value (MJ/kg), Ash melting temperature (°C), Sulfur content (%), Volatile matter content (%), and Carbon content (%).

Results and discussion

The selected chemical and physical characteristics of the produced *Miscanthus* biochar are presented in Table 2.

Table 2

Physicochemical Characteristics of Biochar derived from *Miscanthus* waste biomass

Parameter	Value	Standards for Determination
Specific Surface Area, m ² /g	187	ASTM D-6556
Total Pore Volume by Water, cm ³ /g	0.55	ASTM D-1513
Moisture Content, %	24.9	ASTM D-1509
Volatile Matter Content, %	8.2	ASTM D-1620
Fixed Carbon Content, %	82.5	ASTM D1762-84
Ash Content, %	9.3	ASTM D-1506
Calorific Value, MJ/kg	28.1	ASTM D2015

The biochar's high fixed carbon content, equal to 82.5%, and low volatile matter content, equal to 8.2%, are especially noteworthy, as they indicate the received material's strong stability. These properties make the biochar less likely to degrade over time, which is a key factor for long-term carbon storage in soil. Such stability is essential for effective carbon sequestration, helping to reduce atmospheric levels of carbon dioxide. Compared to other materials, such characteristics make biochar particularly effective in the mitigation of climate change by storing carbon in the soil for extended periods.

Another important feature of biochar is its porous structure, with a total pore volume of 0.55 cm³/g. This enhances the ability of the material to retain moisture, which is especially beneficial for improving soil quality. By increasing the soil's moisture-holding capacity, the biochar helps to maintain more consistent moisture levels, supporting healthier crop growth. The structure also allows biochar to retain nutrients and promote better soil aeration, all of which are beneficial for agricultural productivity. Additionally, the biochar's high calorific value of 28.1 MJ/kg highlights its potential as a renewable energy source. It can be used in bioenergy systems as an eco-friendly alternative to traditional fossil fuels. The combination of high fixed carbon content, developed porous structure, and excellent energy potential makes biochar a highly versatile material with valuable applications in environmental and agricultural fields.

In comparison with findings of other researchers, our results highlighted the effectiveness of *Miscanthus* waste biomass pyrolysis at 600°C. In our experiment, the biochar produced exhibited a specific surface area of 187 m²/g, which is notably higher than the reported earlier value of 90 m²/g [11,12]. This significant increase suggests enhanced adsorption properties, making our biochar a promising candidate for use as a soil additive or in wastewater treatment.

Regarding the fixed carbon content, its value was equal to 82.5%, which surpasses the values reported in other studies (77.7–81.1%). This indicates the efficiency of the applied pyrolysis condition. The high fixed carbon content of biochar is particularly important because it represents stable carbon that can remain in the soil for extended periods, contributing to long-term carbon sequestration efforts.

The volatile matter content of received biochar was 8.2%, which is consistent with values found in other studies [13] (ranging from 6.6% to 7.4%). This suggests an average level of volatile components, typical for biochar produced at 600°C. Additionally, the ash content of received biochar was equal to 9.3% and was lower than the values reported for other biochars, which suggested the potential of *Miscanthus* waste biochar for thermal physico-chemical treatment [14].

Overall, our findings confirmed the high quality of biochar produced from *Miscanthus* pelletized waste biomass at the targeted conditions through oxidative pyrolysis. The combination of high fixed carbon content, low levels of volatile matter and ash, and a substantial specific surface area pointed to the considerable potential of the received biochar to be used as an effective amendment in soil enhancement and climate-related programs.

Conclusions

The biochar produced from *Miscanthus* pelletized waste biomass through oxidative pyrolysis at 600°C shows excellent stability due to its high fixed carbon content (82.5%) and low volatile matter (8.2%), making it an effective long-term solution for carbon sequestration and climate change mitigation. Its porous structure, with a total pore volume of 0.55 cm³/g, enhances moisture retention, benefiting soil fertility and supporting crop growth. With a calorific value of 28.1 MJ/kg, the biochar also holds promise as a renewable energy source, offering an eco-friendly alternative to fossil fuels. Compared to other studies, our biochar's higher specific surface area (187 m²/g) and lower ash content (9.3%) demonstrate its superior quality, making it highly suitable for soil enhancement and various ecological applications.

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Prospects of Sulfur Nanoparticles Application in the Technology of Food Emulsion Systems

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Abstract. *The research focused on optimizing the synthesis of sulfur nanoparticles and exploring their potential use as a substitute for a protein emulsifier in a low-fat, mayonnaise-like model emulsion system. The study evaluated the stability, physicochemical properties, and overall impact of these nanoparticles on the emulsion properties during 30 days of storage.*

Keywords: nanoparticles, sulfur, green synthesis, mayonnaise emulsion, flocculation, viscosity, particle size.

1. Introduction

The last decade has witnessed a significant increase in research on zero-dimensional (0D) sulfur-based nanomaterials. These include sulfur nanoparticles (SNPs), sulfur quantum dots (SQDs), and other 0D nanomaterials, surface-modified or presented as multifunctional nanostructures (core-shell, porous, composite, hybrid, and assembled systems).

0D sulfur-based nanomaterials are of significant scientific interest due to their ease of synthesis, wide range of functionalities, and promising applications in key industrial sectors. They are used in energy storage, photovoltaics, photo- and electrocatalysis, sensing, bioimaging, and biomedical research, and exhibit antifungal and antibacterial activities. In addition, these nanomaterials are used for the separation and concentration of pollutants and as plant growth regulators [1].

Oil-in-water (o/w) emulsion systems are some of the most common in the food industry, pharmaceuticals, cosmetics and pharmaceuticals chemistry. Recently, nanoparticle materials of organic and inorganic nature, including metal oxides, polysaccharide-based materials, silica gels, clay minerals, etc., have been used to stabilise emulsion systems (Pickering stabilisation). Due to the adsorption of solid particles on the surface of the water-oil interface, a structural barrier is formed. It prevents droplet coalescence and further stabilises the system. In general, Pickering emulsions exhibit higher stability than classical emulsion systems that are stabilised with classical surfactants such as proteins and protein-polysaccharide conjugates. The main advantages of pickering-emulsified systems are relatively low production costs, low toxicity, and biocompatibility [2].

The stability of emulsion systems plays a key role in the food, pharmaceutical, and cosmetic industries. It affects the shelf life of the product, its homogeneity, texture, appearance, and consumer properties. It is the stability of emulsions that determines their quality, which is critical for manufacturers and end users. From the point of view of physical colloid chemistry, the stability of emulsions means the stability of their physical and chemical properties for an extended period. Among the mechanisms of destabilisation of emulsion systems are sedimentation, aggregation, coalescence, flocculation, and Ostwald ripening [3]. All of these mechanisms are necessarily

reflected in changes in particle size, shifts in their volume distribution, and changes in rheological characteristics.

Therefore, the aim of the present work was to evaluate the possibility of using biocompatible sulfur nanoparticles to stabilise a model emulsion. Mayonnaise sauce with the addition of canned aquafaba bean as a protein emulsifier was chosen as an emulsion system [4]. It has been shown that the replacement of aquafaba with an aqueous solution of biocompatible sulfur nanoparticles significantly affects the whole range of its physical and chemical properties.

2. Experimental Section

2.1. Materials

L-cysteine, Trisodium citrate dihydrate (later citrate), and Sodium sulfide of high chemical grade (all were purchased from Sigma Aldrich) were used unaltered for the synthesis. All ingredients for the mayonnaise emulsion possessed food-grade quality and were purchased from local producers.

2.2. Synthesis of sulfur nanoparticles under superheated conditions

Sulfur NPs were synthesized using a method developed at the department [5]. Distilled water (28 mL), aqueous solutions of L-cysteine (8 mL, 0.05 M), citrate (2 mL, 0.05 M), and sodium sulfide (2 mL, 0.1 M) were mixed. Then the mixture was heated in a refluxed flask at a temperature of 376 K for 6 h. Samples were taken every 2 h and cooled to room temperature for further measurements. After 4 h of heating, the solution became pale yellow and transparent, and after 6 h, orange-yellow. The pH of the resulting solution was 7.54. The synthesized solution was left to cool and stabilize until the next day.

2.3. Formulation and technology of the model emulsion

For the preparation of the emulsion, the following ingredients were used: refined sunflower oil (30%), mustard powder (1%), dry cream (42% fat) (1%), sulfur nanoparticle solution (5%), sugar (0.5%), salt (1%), baking soda (0.05%), NH pectin (0.4%), xanthan gum (0.3%), carboxymethyl cellulose (0.3%), 9% vinegar (8%), concentrated lactic acid (0.03%), and water. The emulsion was prepared using a classic technique, sequentially combining the hot ingredients, followed by blending the mixture for 5 minutes until an emulsion was formed. A MBL-10-1 blender (MPM, Milanówek, Poland) with a power of 700 W was used for the process.

2.4. Methods

Absorption spectra of sulfur NPs were recorded on a UV-1200 spectrophotometer in a quartz cuvette with an absorbing layer thickness of 1 cm in the wavelength range of 200-700 nm. Photoluminescence spectra of sulfur NPs were recorded using an Ocean Optics USB 650 at an excitation wavelength of 405 nm.

The pH of the nanoparticle solution and the emulsion was determined potentiometrically using a laboratory pH meter, pH-150MI, with a combined electrode ESK-10603pH and a thermal sensor. The pH meter was calibrated using buffer solutions at pH 4.01 and 6.86. To study the viscosity of mayonnaise sauce samples, a rotational viscometer Visco QC (300R) (Anton Paar) with coaxial cylinders CC12 measuring systems was used. All measurements were performed while the system was thermostated at 20 °C (Peltier thermostat PTD 80). Particle size measurement was performed on a particle analyzer – PSA 1190 (Anton Paar). To measure the size of mayonnaise samples, the emulsion was dissolved in warm water (~ 30 °C) in a ratio of approximately 1 g of emulsion to 40 g of water and added to the measuring cell in the portion required to obtain the

required degree of filling of the field of view. Microphotographs were taken using a Micromed microscope with an integrated 1k Pixelink camera and a 60x objective.

3. Results and discussion

3.1. Synthesis of sulfur nanoparticles and characterisation of their optical properties

UV-vis spectroscopy is one of the methods used to determine the stability and formation of sulphur nanoparticles. The measurement of UV absorption in the wavelength range of 250-400 nm is used to confirm the formation of sulfur NPs [6, 7]. The absorption spectra of the sulfur NP solution during the synthesis process are shown in Fig. 1a.

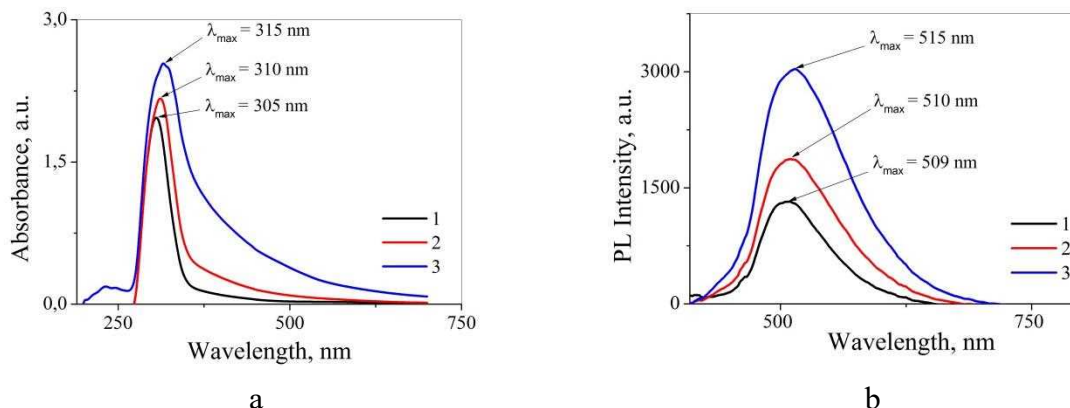


Fig. 1. Absorption and PL spectra (at an excitation wavelength of 405 nm) of sulfur nanoparticles: 1 – after 2 h, 2 – after 4 h, 3 – after 6 h of synthesis (solutions after heat treatment without dilution).

A distinct absorption peak at a wavelength of 305 nm after 2 hours of heat treatment (HT) is associated with the formation of sulfur NPs with polysulfide ions adsorbed on their surface [8, 9]. The absorption peaks for sulfur NPs synthesized in [6] showed absorption in the range of 292–296 nm. As the heat treatment time increases to 4-6 hours, a bathochromic shift of the absorption maxima to 310 nm and 315 nm is observed in the spectra (Fig. 1a), confirming the growth of sulfur NPs during the heat treatment process.

The photoluminescence (PL) spectra of the obtained sulfur NPs are presented in Fig. 1b. The initial solution exhibits no photoluminescent properties, however, after 2 hours of synthesis, a maximum appears at 509 nm in the PL spectra (Fig. 1b), confirming the formation of sulfur NPs in the solution [8, 10, 11]. A further increase in HT duration to 4-6 hours results in a shift of the emission maximum to longer wavelengths – 510 nm after 4 hours and 515 nm after 6 hours, indicating the growth of sulfur NPs, which correlates well with the absorption spectra.

As shown in the PL spectra (Fig. 1b), increasing the HT time from 2 to 6 hours leads to a significant increase in PL intensity due to improved surface passivation of the formed NPs.

During 13 days of storage in a dark place at room temperature, phase separation processes occur in the sulfur nanoparticle solution, which can be observed visually (Fig. 2).

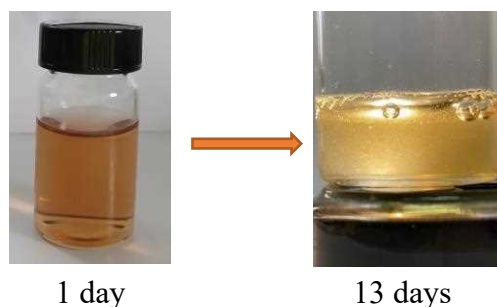


Fig. 2. Destabilization of the sulfur nanoparticle solution during storage.

3.2. Study of the physicochemical properties of mayonnaise emulsion during storage

The emulsion with the addition of sulfur nanoparticle solution holds its shape well, does not flow, and appears sufficiently gelled (Fig. 3). On the 29th day after preparation, no visible signs of emulsion breakdown were observed. Additionally, sulfur nanoparticles synthesized using this method precipitate when the pH shifts toward the acidic side. The pH of the mayonnaise sauce was 3.36, yet the emulsion remained stable throughout the observation period.



Fig. 3. Visual assessment of mayonnaise emulsion stability: 1st vs. 29th day.

To evaluate the structure of the obtained sample, microphotographs were taken (Fig. 3a). It is evident that the emulsion contains both small and a considerable number of large droplets. The micrographs clearly show areas of increased flocculation (highlighted in red). The high degree of flocculation may be associated with the incorporation of sulfur nanoparticles into the mixed polysaccharide-protein layers on the surfaces of oil droplets. The distribution of nanoparticles within the interfacial layers serves as an additional stabilizing factor: in this case, flocculation is controlled, preventing coalescence and emulsion breakdown.

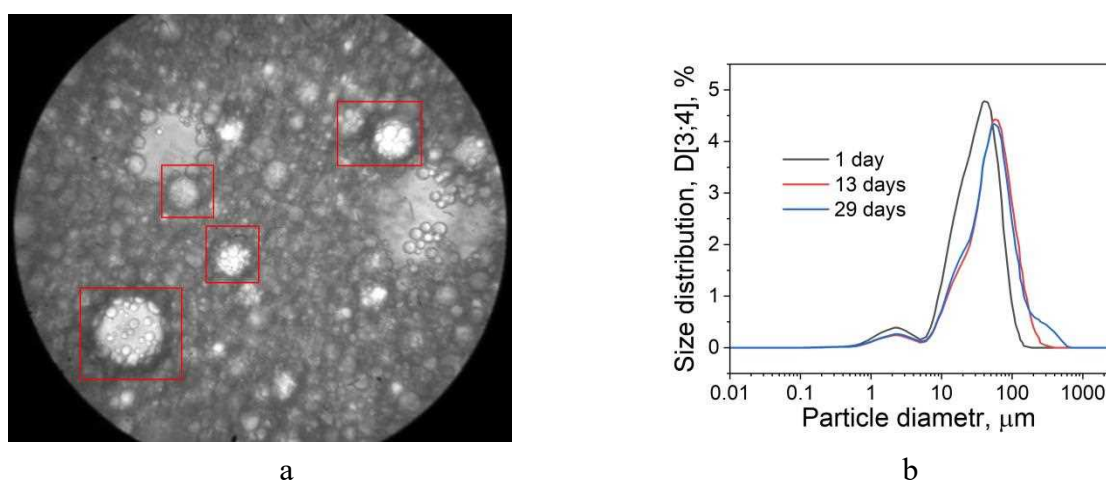


Fig. 4. Microscopic images of mayonnaise emulsion (a) and volume particles size distribution, $D[3,4]$ (b).

From the particle volume distribution curves (Fig. 4b), it is evident that significant changes occurred during the first two weeks of storage. Due to droplet coalescence, the overall peak area increased slightly, and the peaks shifted toward larger droplet diameters. This phenomenon can be explained by flocculation processes occurring in the system during storage. The volume droplet size distribution of the emulsion with legume aquafaba [4] on the first day exhibited a bimodal volume distribution: the first peak, at approximately $2.5 \mu\text{m}$, corresponds to individual droplets, while the second peak, near $8 \mu\text{m}$, characterizes flocculated droplets. During storage, there is a noticeable increase in the number of large particles (D_{90}), which, in turn, affects the average droplet size. This phenomenon is driven by the intensification of flocculation processes (Table 1).

Table 1

Percentile values of the volume droplet size distribution in the mayonnaise emulsion

	D10, μm	D50, μm	D90, μm	D av, μm
1 day	11	39	93	38
13 days	12	45	102	58
29 days	13	52	139	77

The viscosity of the model emulsion remains practically unchanged during storage (Fig. 5). Minor variations in shear stress are observed in the range of 1 to 6 s^{-1} ; however, these are related to changes in flow behavior and are typical for most emulsions of this type. Overall, the observed changes fall within the experimental error, indicating high system stability despite ongoing flocculation processes. Unlike the studied system, the emulsion with the addition of legume aquafaba [4] "flowed"—showing a noticeable decrease in viscosity during the first week. However, its viscosity then stabilized and remained unchanged for 30 days.

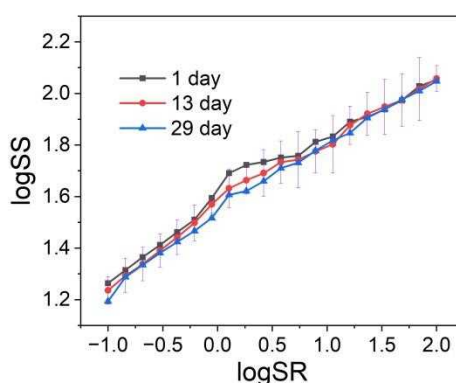


Fig. 5. Dependence of the logarithm of shear stress (SS) on the logarithm of shear rate (SR) for mayonnaise emulsion with added nanoparticles on days 1, 13, and 29.

For both systems, the yield stress and thixotropy index were determined. It was shown that the yield stress for the emulsion with legume aquafaba was **58.8 N/m^2** , while for the emulsion with sulfur nanoparticles, it was **44.4 N/m^2** . The thixotropy index for these emulsions was **688.9 $\text{mPa}\cdot\text{s}$** and **1065 $\text{mPa}\cdot\text{s}$** , respectively. These values can be explained by the fact that in the case of sulfur nanoparticles, more dynamic and adaptive interactions between oil droplets take place, which break more easily under shear stress but recover more quickly once the mechanical impact ceases. Overall, the higher thixotropy index, obtained through a three-step test, indicates that the system is not only stable during storage but also quickly recovers after application or mixing.

Conclusions

The potential application of sulfur nanoparticles in stabilizing a model emulsion system based on 30% fat mayonnaise sauce was demonstrated by incorporating a 5% (by weight) solution of these nanoparticles. Over time, an increase in the average size of fat droplets was observed, attributed to flocculation processes, with the most significant changes occurring within the first two weeks of storage, after which the system reached relative stability. The viscosity of the emulsion remained practically unchanged throughout the observation period, with minor variations in certain shear rate ranges falling within the experimental error and not affecting the overall stability assessment. The flocculation in the system is controlled and does not result in coalescence or emulsion breakdown. Nevertheless, the system remains highly stable, most likely

due to the formation of a Pickering emulsion, where sulfur nanoparticles act as stabilizing agents by being distributed within the adsorption layers on the surface of oil droplets.

Acknowledgments

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La-Modified Cu/ZnO/Al₂O₃ System as the Modern Heterogeneous Catalysts for Water-Gas Shift Process

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Abstract. *The role of applied catalysis in the modern chemical industry, with a special emphasis on the requirements for novel catalysts, has been presented. On the basis of years of INS, the problems of development and requirements for modern catalysts. In order to fulfill strict process requirements and to enhance the stability of low-temperature WGS (LT-WGS) catalysts, scientific research on the improvement of the catalyst is carried out. The effect of lanthana addition to CuZnAl hydroxycarbonate precursor on the crucial physicochemical parameters and stability of catalytic activity was studied. Finally, the efficiency of a pilot batch of La-modified CuZnAl catalyst was tested. The results of investigations on improving catalysts for water-gas shift reaction widely used in crucial branches of syngas and hydrogen industry were shown, and the role of proper transition from laboratory through large-laboratory scale to TRL 9 has been emphasized.*

Keywords: WGS, syngas, hydrogen, catalyst, Cu/ZnO/Al₂O₃, lanthana, modifier.

Introduction

The Cu/ZnO/Al₂O₃ catalysts have found many applications in the C₁ chemistry, mainly in the low temperature water-gas shift reaction ($\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2$) (LT-WGS) as well as in methanol synthesis and processing [1]. The improvement of well-known catalysts and The development of new-generation catalytic systems remains a very important element of strategy to meet environmental and technological requirements. The requirements of high-quality modern LT-WGS catalysts are:

- active at low temperature, high selectivity, high and accessible surface area capacity per unit volume,
- low and stable pressure drop, resistance to operational accidents - high mechanical strength,
- stable activity during the whole catalyst lifetime, high resistance to catalyst poisoning, and long catalyst lifetime.

Many studies reveal the potential of lanthana as a modifier of alumina, mixed oxides, and supports of metallic catalysts. Although investigations on the effects of lanthana on the Cu/ZnO/Al₂O₃ catalysts' properties are relatively sparse. Only a few literature reports indicate that the improvement of catalyst stability can be achieved by doping the conventional Cu/ZnO/Al₂O₃ catalyst with lanthana [2,3]. In this work, CuZnAlLa catalysts of different Cu/Zn and Al/La molar ratios were prepared using a simple co-precipitation with aqueous solutions of Cu, Zn, Al nitrates, with Na₂CO₃ and NaOH at various pH, with subsequent thermal treatment of the resulting precursors. It was shown using XRD that synthesized precursors are CuZnAlLa-hydroxycarbonates with a dominant content of hydrotalcite-like phase. The oxide form of catalysts has been analyzed using various characterization techniques such as XRF, XRD, TPR, and chemisorption techniques. The performance of all catalysts was evaluated in the kinetic regime

using a Tiomkin-type differential reactor. In the result of scaling up process the technical batch of the CuZnAlLa catalyst was synthesized and formed into different grain shape. The comprehensive activity and stability measurements were carried out using gradientless reactor with mixing at the test conditions similar to LT-WGS process in syngas plants. Finally the results of pilot batch performance in industrial reactor were shown and compared with lanthana-free standard catalyst.

Characterization

Chemical compositions of samples were determined by the XRF method using a X'UNIQUE II – Philips spectrometer. The XRD measurements of the precursor were performed on a PANalytical Empyrean. The BET was determined using a Micromeritics ASAP® 2050 Xtended Pressure analyzer.

The TPR analysis was performed using a Micromeritics AutoChem 2950HP instrument. A catalyst sample (ca. 25 mg fraction of 0.1–0.2 mm) was placed in a U-tube reactor and treated in a flowing 5% H₂/Ar mixture (40 mL/min) with a temperature increase of 5 °C/min up to 800 °C. The effluent gas was passed through a dry ice bath to freeze out water. Changes of H₂ concentration in effluent gases were measured by a thermal conductivity detector (TCD).

The LT-WGSS activity tests were performed using a Tiomkin-type differential reactor (at a conversion degree below 0.1). In the initial step, the samples were *in-situ* reduced by heating to 240 °C at 1 °C/min and stabilized at 240 °C/4h. In the next step, reducing gas was replaced with a reaction mixture of process gas saturated with steam. Tests were carried out under conditions: 2.5 MPa, 180–240 °C. The effluent gases were first passed through a cold trap to remove water, and then dry gases were analyzed using an online GC equipped with a methanizer and FID detector. The reaction rate was calculated on the basis of the mass balance of the reactor.

Results

It was shown that the catalysts are meso- and macroporous systems with a favorable, high specific surface area development. Obtaining the volume of pores (TPV), including mesopores (V_m), and a higher degree of specific surface area development (S_{BET}) is favored by conducting the synthesis at a higher Na₂CO₃/NaOH ratio. Favorably high values of active copper surface area (S_{Cu}) are obtained for catalysts whose precursors were synthesized at a higher Na₂CO₃ content - Table 1.

Table 1

Chemical composition and physicochemical properties of CuZnAlLa samples

	Chemical composition wt. %				S _{BET} [m ² /g]	TPV, [ml/g]	V _m [ml/g]	S _{Cu} [m ² /gCu]
	CuO	ZnO	Al ₂ O ₃	La ₂ O ₃				
CZAL_1_1	45.7	29.0	18.6	0.0	55.8	0.17	0.11	20.9
CZAL_2_1	47.2	24.9	13.2	2.6	78.4	0.36	0.24	28.8
CZAL_3_1	41.9	27.3	11.5	5.6	78.1	0.51	0.31	45.8
CZAL_4_2	45.2	29.4	18.0	0.0	64.5	0.33	0.17	20.8
CZAL_5_2	43.6	27.8	14.4	3.1	68.8	0.45	0.26	36.8
CZAL_6_2	45.5	27.0	12.7	5.4	85.3	0.46	0.29	37.7
CZAL_7_4.7	48.8	29.3	16.2	0.0	72.7	0.35	0.22	27.1
CZAL_8_4.7	43.7	29.3	14.1	2.9	84.0	0.41	0.28	42.3
CZAL_9_4.7	45.7	26.8	11.2	5.4	76.7	0.39	0.27	39.4

The results of activity tests in the kinetic regime (Fig. 1) indicate very high activity of all La-doped catalysts. It should be emphasized that the highest low-temperature activity was

demonstrated in the case of the systems containing more than 2 wt.% La_2O_3 synthesized at an increased $\text{Na}_2\text{CO}_3/\text{NaOH}$ ratio (preferably more than 2). The similar slopes of Arrhenius plots indicate similar activation energy values. La doping therefore promotes catalyst activity not by changing the reaction mechanism but by creating or increasing the availability of surface active centers.

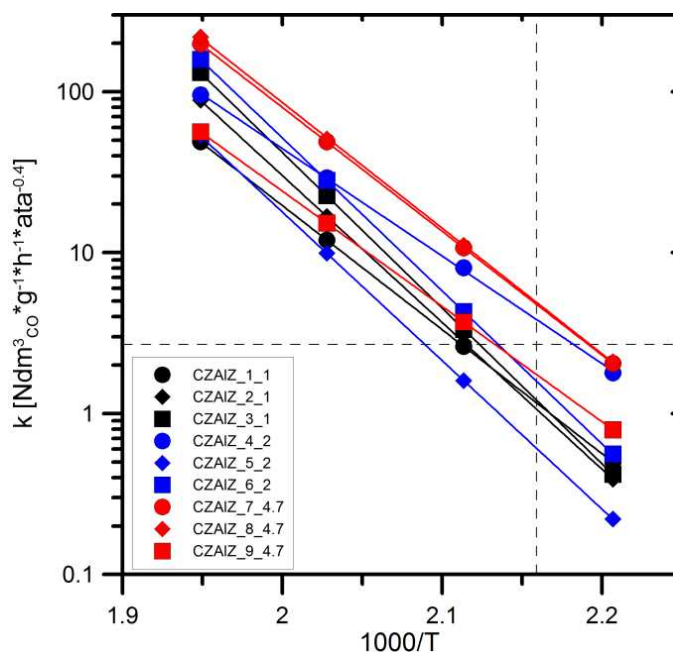


Fig.1. Arrhenius plot for comparison of catalysts' activity.

In the next step, the catalysts of the proper formula were scaled up. The semitechnical batch (20 kg) of the catalyst was synthesized in the pilot plant. Catalytic material was formed into functional shapes of different sizes and geometries by tableting. The pilot batch of the catalyst was deeply investigated, and its high quality and effectiveness have been confirmed. Finally, the production batch of the new catalyst was produced and placed in the industrial LT-WGS reactor of the ammonia plant for a test run under real industrial-scale process conditions. Mathematical analysis of operational data from the test batch operation confirms the high activity of the La-modified $\text{Cu}/\text{ZnO}/\text{Al}_2\text{O}_3$ catalyst and its favorable hydrodynamic properties in the LT-WGS process. At the inlet process gas temperature to the LT-WGS bed of about 220 °C, pressure of 2.77 MPa, and gas load of 6570 h^{-1} , the exotherm is relatively sharp and is located mainly in the inlet and middle part of the bed. The trial charge of the new LT-WGS catalyst has been in operation for over 3 years in the NH_3 plant. Operational data shows a sharp exotherm profile, high activity, and a lower rate of the exotherm movement along the length of the catalyst bed compared to the previous charge operated during the previous campaign.

Analysis of operational data proves a very good performance and quality of the new catalyst. Thanks to this, better technological parameters (CO conversion, low deactivation rate) were obtained as compared to catalysts previously exploited in the same plant. The expected high-performance lifetime of the new trial charge is very long. Properties of novel catalyst:

- high and stable activity due to optimized catalyst formula - Cu dispersed in specific oxide matrix,
- good poison retention at the inlet section of the bed, self-guarding properties,
- high crush strength of fresh as well as catalyst pellets after reduction.

Benefits of novel catalysts:

- possible to carry out the LT-WGS process under more thermodynamically favorable conditions with very low ATE,
- high crush strength and durability of catalyst pellets after reduction, leading to increased tolerance to operational upsets,
- low rate of the exotherm moving along the bed,
- safe and long service life without catalyst replacement.

Conclusions

It has been shown that CuZnAlLa hydroxycarbonates with a dominant share of hydrotalcite analogue are good precursors of LT-WGS catalysts. Doping the Cu/ZnO/Al₂O₃ catalyst with lanthana has a very beneficial effect on the physicochemical properties, and above all on the pore system and the development of the active Cu surface area. This directly leads to an increase in catalytic activity. It turned out to be particularly advantageous to conduct the synthesis of the precursor at a high Na₂CO₃/NaOH ratio and lanthana addition at a level of over 2 wt.%. The industrial pilot batch of LT-WGS catalyst obtained on the basis of laboratory and scaling-up results has been operated for almost 4 years in a highly effective manner. The example of a syngas plant for ammonia production illustrates mutual correlations between process engineering and applied catalysis. Numerous other examples of important industrial processes can be given, the realization of which would be impossible without the application of catalysts. Progress is the result of modern chemistry, process engineering, and the design of new catalysts with the required properties. Due to chemical industry requirements, basic research and implementation works in the domain of applied catalysis are focused on:

- implementation of new types of catalysts of high activity on the unit of bed volume, allowing for exploitation at high load,
- catalyst selectivity improvement - products with minimal quantity of by-products,
- development of catalytic combinations useful for different raw feedstock processing and characterized by high resistance to poisons,
- development of catalysts with a lower content of precious metals and search for entire replacement of precious metals,
- development of ecological technologies for catalyst production and spent catalyst utilization technologies.

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New Types of Cold-Applied Bituminous Roofing Materials

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Abstract. *In this work, a three-component bitumen composition was developed that can be used for the production of cold-applied rolled bitumen roofing materials. The advantage of this composition is its availability and relatively low cost due to the use of rapeseed oil.*

Keywords: bitumen, rapeseed oil, bitumen composition, roofing material, adhesion, elasticity.

Introduction

The advantage of cold-applied bituminous roofing materials is that they are easy to apply, do not require special surface preparation, and have a relatively low cost, short preparation time, and easy repair. The disadvantage of all materials made with bitumen is their short life. Therefore, bituminous materials used to produce cold-applied roofing materials should be characterized by good elasticity, high heat resistance, flexibility at sub-zero temperatures, and high adhesion to hard surfaces.

In previous studies, three-component bituminous compositions were developed, which include bitumen, rubber or rubber crumb, and linseed oil [1]. However, in our opinion, flaxseed oil is not the best option, as it is quite expensive and produced in limited quantities. Therefore, it is relevant to study the possibility of replacing this oil with a cheaper and more affordable one. This will make it possible to reduce the cost of the final product without compromising its quality.

Results and Discussion

Commercial bitumen of BN 70/30 grade was used as the basis for obtaining three-component bitumen compositions, which will be used in the production of cold-applied rolled roofing materials in the future (Table 1). Rapeseed oil was used as a component to impart adhesive properties to the composition. As a plasticizer, we used the Kraton D1192ESM modifier, which is a block copolymer of the styrene-butadiene-styrene (SBS) type.

Table 1

Characteristics of bitumen BN 70/30

Indicator	Value of the indicator
Softening temperature by “ring and ball”, °C	82
Ductility at 25 °C, cm	2
Penetration at 25 °C, 0.1 mm	17
Elasticity, %.	50

The preparation of bitumen compositions was carried out in a laboratory mixing unit. To prepare the compositions, pre-weighed samples of the initial components were loaded into a metal container and heated with constant stirring. The performance of the resulting compositions was determined by standardized methods.

The possibility of obtaining cold-applied bituminous materials was initially studied by examining binary mixtures obtained by mixing two components: construction bitumen BN 70/30 and rapeseed oil at temperatures of 170-190°C for 1 hour (Table 2).

Table 2

Influence of rapeseed oil content on the properties of a binary mixture “bitumen: rapeseed oil”

Indicator	Bitumen BN70/30	Rapeseed oil content, % wt.		
		10	15	20
Softening temperature, °C	82.0	66.0	55.0	51.0
Ductility at 25 °C, cm	2.0	4.7	7.8	8.1
Penetration at 25 °C, 0.1 mm	17.0	45.0	62.0	75.0
Elasticity, %.	50.0	37.0	26.0	21.0
Low-temperature flexibility at -25 °C	fails the test	fails the test	fails the test	stands the test
Heat resistance at 60 ° C	stands the test	fails the test	fails the test	fails the test
Adhesion, N/cm ²	–	3.2	5.8	5.1
Water absorbing, %	0.06	0.11	0.16	0.19

The studies have shown that with an increase in the content of rapeseed oil in binary mixtures with bitumen, the softening point and elasticity decrease, and the penetration increases. It was found that the addition of rapeseed oil to bitumen increases its adhesion to hard surfaces. At the same time, the effect of “stickiness” of the bitumen material at room temperatures is observed, which allows its use without preheating.

As a result of studying the properties of the binary mixture “bitumen: rapeseed oil”, it was found that it is impossible to obtain a bituminous material that meets all the requirements based on these two components alone. To the studied binary mixture, it is necessary to add a component that would increase the hardness and softening point of the bitumen material, while increasing its elasticity and frost resistance, and not worsening other indicators. It is known that this effect is achieved when rubbers, in particular SBS, are added to bitumen. That is why it was necessary to study the properties of a three-component mixture containing BN 70/30 bitumen, rapeseed oil, and SBS rubber in different proportions.

The results of the study of the three-component mixture “bitumen: rapeseed oil: SBS rubber” are given in Tables 3-5. It was found that an increase in the content of SBS rubber in the three-component mixture significantly increases its softening point and elasticity, as well as reduces penetration. That is, the introduction of rubber into the mixture increases the refractoriness and hardness of the resulting composite material. This is confirmed by an increase in the heat resistance of the bitumen composition due to the addition of SBS rubber to it. The composition's ductility changes insignificantly, given the low ductility of the original BN 70/30 bitumen. The same can be said about the water absorption of the three-component bitumen composition.

However, there is a negative side to adding SBS rubber, which is a decrease in adhesion. With an increase in the content of SBS rubber in a three-component bitumen composition, it adheres much worse to a hard surface and comes off with less force.

Table 3

Characterization of the three-component composition "bitumen: rapeseed oil: SBS"
(rapeseed oil content 10% by weight)

Indicator	Bitumen BN 70/30 + 10% RO	SBS content, % wt.		
		3	5	10
Softening temperature, °C	66	76	82	94
Ductility at 25 °C, cm	4.7	5.6	6.2	7.3
Penetration at 25 °C, 0.1 mm	45.0	40.0	37.0	29.0
Elasticity, %.	37.0	56.0	66.0	85.0
Low-temperature flexibility at - 25 °C	fails the test	fails the test	fails the test	fails the test
Heat resistance at 60 ° C	fails the test	stands the test	stands the test	stands the test
Adhesion, N/cm ²	3.2	2.8	2.3	1.4
Water absorbing, %	0.11	0.12	0.12	0.14

Table 4

Characterization of the three-component composition "bitumen: rapeseed oil: SBS"
(content of rapeseed oil 15 % by weight)

Indicator	Bitumen BN 70/30 + 10% RO	SBS content, % wt.		
		3	5	10
Softening temperature, °C	55	63	69	78
Ductility at 25 °C, cm	7.8	8.5	9.0	9.6
Penetration at 25 °C, 0.1 mm	62.0	57.0	52.0	41.0
Elasticity, %.	26.0	40.0	51.0	72.0
Low-temperature flexibility at - 25 °C	stands the test	stands the test	stands the test	fails the test
Heat resistance at 60 ° C	fails the test	fails the test	stands the test	stands the test
Adhesion, N/cm ²	5.8	5.2	4.6	3.2
Water absorbing, %	0.16	0.17	0.18	0.20

Analyzing the results obtained, the optimal composition of the mixture was determined, which ensures the achievement of the required quality standards for cold-applied bitumen material. It was found that the content of BN 70/30 bitumen in such a composition should be 82.5 % by weight, the content of rapeseed oil - 12.5 % by weight, and the content of SBS - 5.0 % by weight. Based on the established optimal composition, a bitumen composition for cold-applied materials was obtained. The characteristics of this composition are given in Table 6.

The developed bitumen composition for cold-applied roofing material meets all the requirements.

An approximate calculation of the cost of marketable products of the three-component bitumen compositions production unit was made. The calculated cost is 22,155 UAH/t, which is commensurate with the cost of industrial analogs.

Table 5

Characterization of the three-component composition "bitumen: rapeseed oil: SBS"
(content of rapeseed oil 20 % by weight)

Indicator	Bitumen BN 70/30 + 20% RO	SBS content %.		
		3	5	10
Softening temperature, °C	51	58	63	72
Ductility at 25 °C, cm	8.1	9.0	9.6	10.4
Penetration at 25 °C, 0.1 mm	75.0	68.0	62.0	50.0
Elasticity, %.	21.0	32.0	41.0	59.0
Low-temperature flexibility at - 25 °C	stands the test	stands the test	stands the test	stands the test
Heat resistance at 60 ° C	fails the test	fails the test	stands the test	stands the test
Adhesion, N/cm ²	5.1	4.5	4.0	2.6
Water absorbing, %	0.19	0.19	0.20	0.21

Table 6

Characteristics of the bitumen composition "bitumen: rapeseed oil: SBS"
for cold applied roofing material

Indicator	The value of the indicator	Requirements for bituminous material
Softening temperature, °C	70	not less than 70
Ductility at 25 °C, cm	9.2	—
Penetration at 25 °C, 0.1 mm	50.0	—
Elasticity, %.	53.0	—
Low-temperature flexibility at - 25 °C	stands the test	stands the test
Heat resistance at 60 ° C	stands the test	stands the test
Adhesion, N/cm ²	4.5	not less than 3.0
Water absorbing, %	0.18	—

Conclusions

A method for obtaining a three-component bitumen composition for the production of cold-applied rolled roofing materials that meets all the requirements for these materials has been developed. The optimal composition of such a mixture was determined: bitumen BN 70/30 - 78.5 % by weight, rapeseed oil - 12.5 % by weight, SBS - 5.0 % by weight.

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Luminescent Determination of 4-Nitrophenol in Water Using AgInS₂ and CuInS₂ Nanoparticles

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Abstract. *AgInS₂ and CuInS₂ stable colloids were prepared, and the photoluminescence and absorption spectra of these nanoparticles were obtained. AgInS₂ nanocomposite films were made by the layer-by-layer deposition method. It was found that 4-nitrophenol significantly reduces the photoluminescence intensity of AgInS₂ and CuInS₂ even at the lowest concentration of 0.1 mg/l.*

Keywords: nanoparticles, photoluminescence, 4-nitrophenol, AgInS₂, CuInS₂.

Introduction

Quantum dot synthesis technology has made a major breakthrough in practical applications and has achieved significant progress in commercial displays (QLED), saving energy, biosensors, photocatalysis, etc. [1-3]. I-III-VI AgInS₂ and CuInS₂ nanocrystals have a number of advantages, such as low cost and easy synthesis, and the main one is the absence of highly toxic (Cd, Pb) elements compared to other QDs [4-6]. Nanocrystals of this type have previously been used as a detector of pollutants, for example, heavy metals [7]. Sensors have revolutionized engineering systems due to their ability to detect changes in the environment, providing feedback to other electronic components. A current trend in the development of electronic sensor devices is the use of various types of nanomaterials to miniaturize and increase the sensitivity of sensors. Due to their mobility and naked eye visibility, fluorescent explosive sensors are widely used for the detection of explosives in water, organic solvents, and the gas phase. Nanomaterials have emerged as key players in sensor technologies due to their inherent optical properties, exceptional surface chemistry, unique wavelength tunability, and high quantum yield, which combine their selective sensing ability with a low detection limit and fast response [8]. The development of effective methods for detecting nitro compounds is an important step in solving the problem of environmental safety. An urgent task is to detect water contamination by organic residues, surfactants, pesticides, phenol compounds, in particular, p-nitrophenol. The creation of sensors based on AgInS₂ or CuInS₂ nanoparticles will allow monitoring soil and water contamination, taking timely measures to prevent negative consequences, and ensuring human health and environmental preservation.

Experimental

The synthesis of CuInS₂ nanoparticles was carried out in a flask with active stirring. 20 ml of distilled water, 1 ml of CuSO₄ solution, 0.04 ml of InCl₃ solution, and 0.4 ml of Na₃Cit solution were added to the flask. After further addition of 10 µl of TGA and 62 µl of Na₂S, the solution acquired a reddish-brown color, followed by heating the solution in a water bath at 80°C for 30 min. A 4-nitrophenol solution with a concentration of 1 g/l was diluted 10, 20, 40, 100, and 1,000 times.

The AgInS₂ nanoparticles colloids were obtained by a one-step synthesis method [9]. The AgInS₂ colloidal solution with the ratio In: Ag = 5, with a maximum of PL in the red region of the

spectrum (605 nm), was chosen for the production of nanocomposite films by the layer-by-layer deposition method reported earlier in [10].

Results and discussion

The reddish brown CuInS_2 nanoparticles with PL maximum located at 700 nm were obtained at the ratio $[\text{In}]/[\text{Cu}] = 4$. The photoluminescence intensity of CuInS_2 NPs in the solution significantly decreases with increasing concentration of 4-nitrophenol from 0 to 10 mg/l (Fig.1). It was investigated in [11] that due to the electron-withdrawing nitro groups in the benzene ring, nitroaromatics with low energy of empty π^* orbital are good acceptors of electrons, so electron-rich luminescent nanomaterials (CdSe/ZnS QDs) can be strongly quenched by nitroaromatics via photo-induced electron transfer (PET) or fluorescence resonance energy transfer (FRET). Control experiments with phenol did not show any photoluminescence quenching, which once again confirms the effect of the nitro group on reducing the intensity of photoluminescence of colloid CuInS_2 semiconductor nanocrystals.

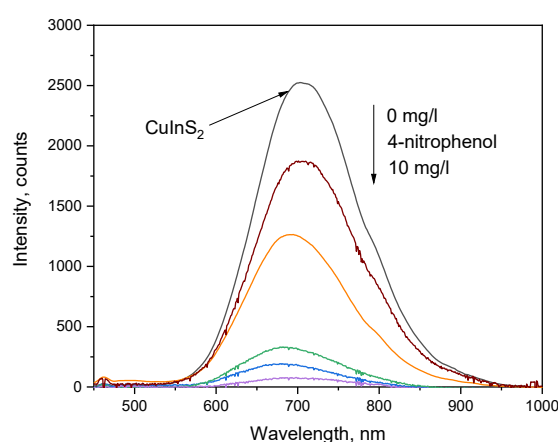


Fig. 1. Change in PL intensity of colloid CuInS_2 semiconductor nanocrystals depending on the concentration of 4-nitrophenol.

From the results of measuring the optical density (ABS) of the studied solutions, it was found that the optical density value decreases with the addition of 4-nitrophenol to the initial CuInS_2 nanoparticles colloids (Fig. 2). Since 4-nitrophenol also absorbs in this spectral region, it is difficult to determine the effect of the nitro group on the optical density values of CuInS_2 nanoparticles solution.

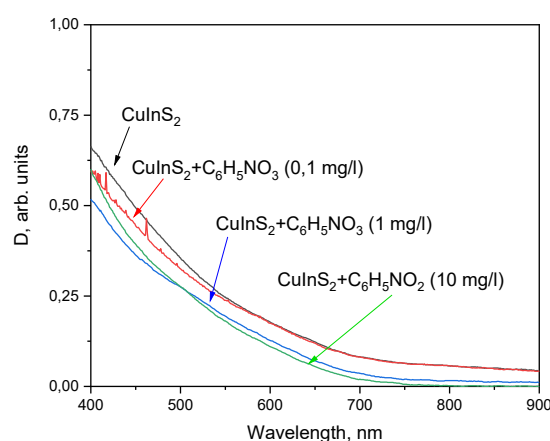


Fig. 2. Absorption spectra of CuInS_2 NP colloids

To study the sensor properties of the AgInS₂ nanocomposite films, the PL spectra were measured before and after immersion in a solution with different concentrations of the analyte. The spectra were normalized relative to the intensity of the lamp spectrum with which the samples were irradiated (405 nm). Fig. 3 shows the change in the PL intensity of the sensor based on the polycationic film and AgInS₂ semiconductor nanocrystals depending on the content of 4-nitrophenol. It is obvious that even at a low concentration of 4-nitrophenol (0.25 mg/ml) in the solution, there is a significant decrease in the intensity of the PL peak. These measurements indicate that these films, as CuInS₂ colloids, can be used for the production of luminescent sensors.

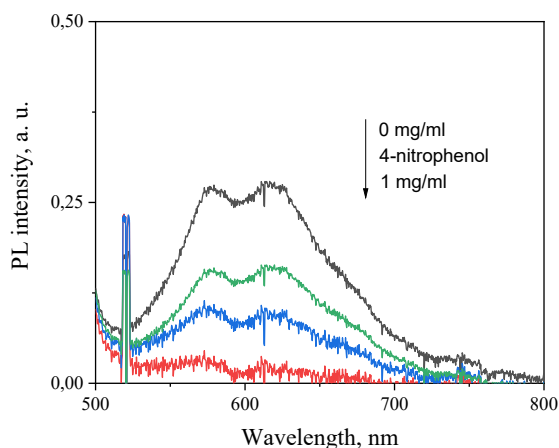


Fig. 3. Change in the PL intensity of the sensor based on a polycationic film and AgInS₂ semiconductor nanocrystals depending on the concentration of 4-nitrophenol.

The concentration dependence of the PL peak area of the sensor based on a polycationic film and AgInS₂ semiconductor nanocrystals on the concentration of 4-nitrophenol is presented in Fig. 4. The tendency to decrease the PL peak area with increasing 4-nitrophenol concentration is observed even with a small content of 4-nitrophenol.

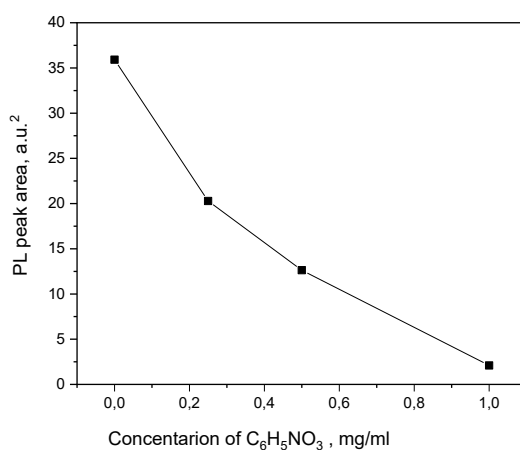


Fig. 4. Concentration dependence of the PL peak area of the sensor based on a polycationic film and semiconductor nanocrystals AgInS₂ on the content of 4-nitrophenol.

Conclusions

1. AgInS₂ and CuInS₂ nanoparticles were synthesized by the hydrothermal method to obtain stable colloidal solutions for at least one month with no detectable degradation.
2. It was found that the -NO₂ group in the benzene ring of 4-nitrophenol noticeably quenches the photoluminescence of AgInS₂ and CuInS₂ nanoparticles.

3. It was determined that the minimum concentration of 4-nitrophenol in the solution, at which a significant change in intensity occurred, was 0,1 mg/l.

Thus, the simplicity of the detection method, and particularly, the ability to use QD films for localized detection of explosives, supports potential future applications of these systems.

Acknowledgments

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Selenium-Modified Microgels: Novel Catalysts for Cross-Phase Oxidation of Aromatic Aldehydes

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Abstract. *This paper explores selenium-modified microgels as interfacial catalysts for the environmentally friendly oxidation of aromatic aldehydes. Using mild reaction conditions and hydrogen peroxide as a green oxidant, microgels demonstrate versatility across various aldehydes and solvent systems while offering excellent reusability, positioning these microgels as promising candidates for sustainable oxidation processes.*

Keywords: microgels, selenium, interfacial catalysis, oxidation, aromatic aldehydes, heterophase reaction, green chemistry, sustainable synthesis.

Introduction

Oxidation reactions are crucial in various chemical processes, from industrial synthesis to environmental remediation. The development of efficient and sustainable catalytic systems remains a significant challenge. Heterogeneous catalysts offer numerous advantages over homogeneous catalysts, including separation, recovery, and recycling capabilities, which make them more environmentally friendly as they produce fewer pollutants. However, homogeneous catalysts typically offer better accessibility to catalytic sites and higher product selectivity.

Performing reactions under biphasic ("water-oil") conditions can facilitate product separation and purification, especially when the starting material and product reside in different phases [1]. The growing interest in these systems stems from their environmentally friendly conditions, particularly when reactions occur in aqueous media. However, the poor water solubility of many organic reactants presents a challenge. While surfactants can facilitate such reactions, separating them from products and catalysts for reuse can be difficult. An ideal solution would be a heterogeneous catalyst with surfactant properties [2].

Here, we explore the performance of the Se-modified microgels [3] in emulsion stabilization and investigate their catalytic activity in the oxidation of aromatic aldehydes in oil/water biphasic systems. Oxidation of aromatic aldehydes, such as benzaldehyde, anisaldehyde, and cinnamaldehyde, to the corresponding acids represents an important pathway in chemical valorisation for the synthesis of valuable products and intermediates. Aromatic aldehydes generally are not soluble in water, so performing the reaction in heterophase conditions using an interfacial catalyst should be beneficial to facilitate their oxidation with hydrogen peroxide.

Results and Discussion

The hydrodynamic radii (R_h) of Se-modified microgel structures can affect their catalytic performance. In water, poly(N-vinylcaprolactam)-based microgels are swollen below the Volume Phase Transition Temperature (VPTT, $\sim 32^\circ\text{C}$). Above the VPTT, the microgels transform into a collapsed state. In contrast, in toluene solution, microgels remain swollen regardless of temperature (Fig. 1a).

The microgel caused a dramatic reduction of the interfacial tension (up to 42-fold reduction) compared to the reference (Fig. 1b). With increasing temperature, a slight increase in interfacial tension was observed, which has been attributed to the aggregation of polymer chains.

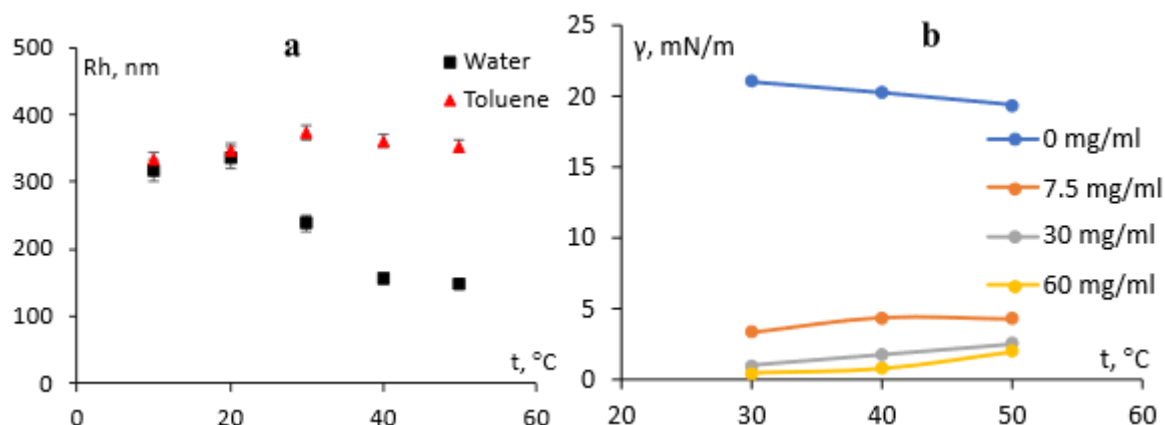


Fig. 1. a) Hydrodynamic radii of Se-modified microgel in toluene and water. b) Dependence of interfacial tension (γ) in toluene-water on temperature and concentration of Selenium-modified microgel.

Confocal images (Fig. 2) show the formation of toluene droplets inside of the water phase. With the increase of the microgel concentration from 15 to 30 mg/ml, the size of the droplets decreases. These results are in good agreement with a previously published study [4] where it was shown that for emulsions undergoing limited coalescence, the total number of particles is inversely proportional to the droplet size. However, a linear dependence is generally observed at low particle concentration. When particles are in excess, the linearity is lost, and the obtained emulsions become very polydisperse ($P > 30\%$).

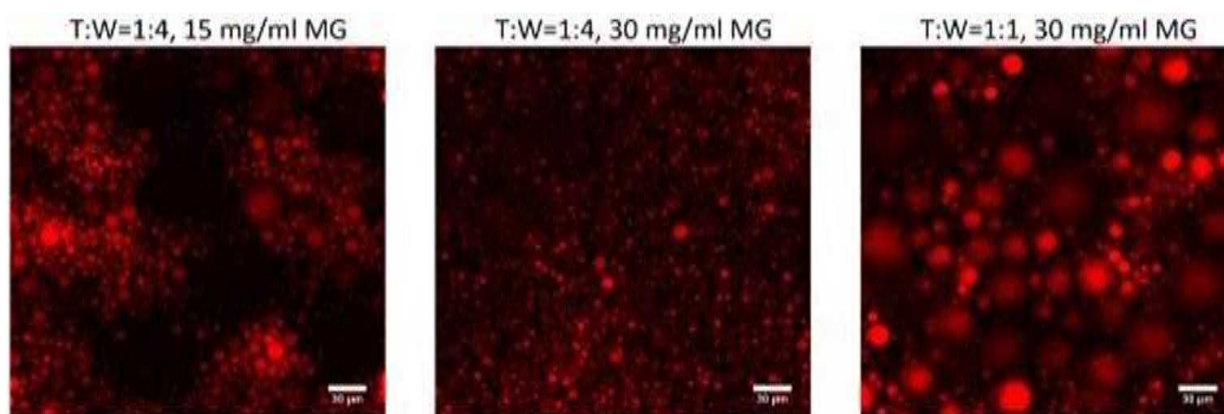


Fig. 2. Confocal images of toluene/water emulsions stabilized by Se-modified microgel. Toluene (T): Water (W) ratio 1:4 and 1:1, microgel (MG) concentration 15 and 30 mg/ml. Nile red was used as a dye (soluble only in toluene).

In this limit, the size distribution is less sensitive to the total particle amount and depends mainly on the stirring intensity [4]. Previously, PNIPAm microgels (1.5% BIS) with microgel concentrations in the emulsion in range of 0.01–0.1%wt were used, while, in our case, concentrations were in the range of 1.5–3%wt. This explains the high polydispersity of droplet sizes in our case.

The catalytic activity of Se-modified microgels was evaluated in a model reaction of benzaldehyde oxidation with hydrogen peroxide under biphasic (toluene/water) reaction conditions. The oxidation occurs at the interface between the toluene phase (containing benzaldehyde) and the water phase (containing hydrogen peroxide), with the selenium-containing microgel acting as an interfacial catalyst due to its surfactant properties and catalytic seleninic groups. Phenol (as a result of full oxidation of the aldehyde group) was the sole by-product in the benzaldehyde oxidation at all reaction conditions.

The catalytic activity of the Se-modified microgel increases with reaction temperature up to 50°C (Fig. 3a). A further increase in temperature results in a lower benzoic acid yield, correlating with the thermal responsiveness of the microgel in water. At temperatures higher than 40°C, the hydrodynamic radius of the microgel in water is 2 times smaller than at 20°C, which may cause a slowdown in the reagent diffusion rate inside the microgel particles [5].

When the reaction was performed in media with a large excess of water, the yield of benzoic acid and the reaction rate were quite low. As the amount of water in the reaction mixture was reduced from 80% (T1W4) to 20% (T4W1), both the reaction rate and the benzoic acid yield increased significantly. For the reaction performed with a T:W ratio of 4:1, the Se-microgel proved to be a highly active colloidal catalyst, achieving a yield of 95.6% of benzoic acid at 50°C.

The yield of benzoic acid increases rapidly with the reaction time up to 88.8% at 5 hours (Fig. 3b). Further increase of the reaction time to 8 hours leads to a relatively smaller increase in yield to 95.6%, which is not very efficient in terms of productivity, but has the additional benefit of increasing the selectivity from 91.2% to 96.6%, which is much more valuable. Therefore, 8 hours was chosen as the optimal reaction time.

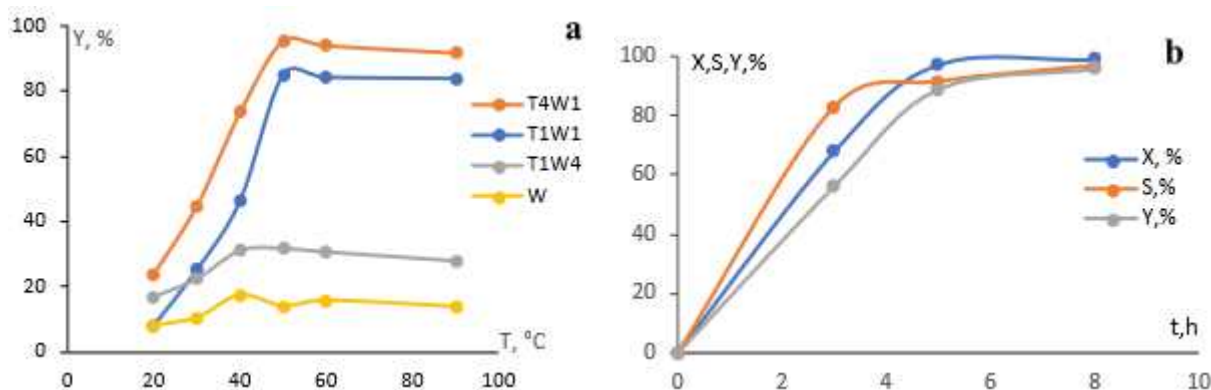


Fig. 3. a) Effect of toluene: water ratio and reaction temperature on the yield of benzoic acid (Y).

b) Effect of reaction time on the yield of benzoic acid (Y). Catalyst – B1.5Se2.0.

Besides toluene, the microgel catalyst was tested in chloroform, ethyl acetate, and 1-octanol in water emulsions with a solvent:water ratio of 4:1 (Fig. 4). All of these provided lower yields of benzoic acid compared to the toluene/water system: 70.9% in chloroform/water, 53.6% in ethyl acetate/water, and 25.5% in 1-octanol/water. Interestingly, in the 1-octanol/water system, octyl benzoate (23.3%) was obtained alongside benzoic acid, suggesting either oxidative alkoxylation of benzaldehyde or subsequent esterification of benzoic acid, with a total oxidation yield of 48.8%.

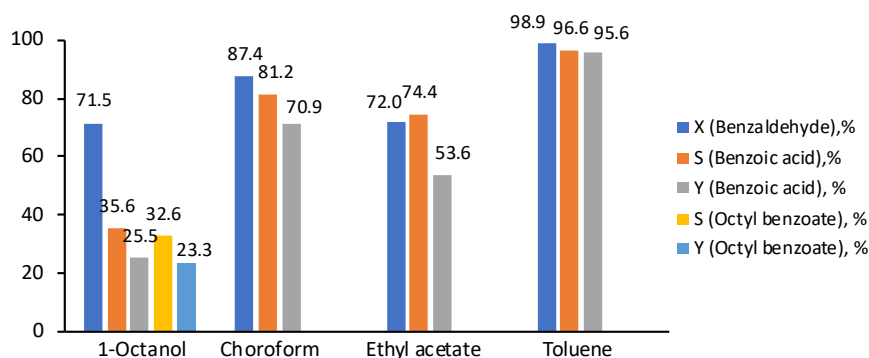


Fig. 4. Effect of solvent nature on the yield of benzoic acid (Y). Solvent:water ratio=4:1. Reaction temperature – 50 °C. Reaction time – 8 h.

In addition to benzaldehyde, cinnamaldehyde, anisaldehyde, and veratraldehyde were investigated in the toluene/water (4:1) system (Fig. 5). The Se-microgel catalyst proved active in oxidizing these aldehydes too, but with lower selectivity for the corresponding acids. Cinnamaldehyde oxidation produced 29.8% cinnamic acid, 9.8% hydrocoumarin, and 17.1% benzoic acid. Anisaldehyde oxidation yielded 28.5% anisic acid and 35.2% mequinol. Veratraldehyde oxidation produced only 1.7% veratric acid, with the main product being 3,4-dimethoxyphenol (39.0%).

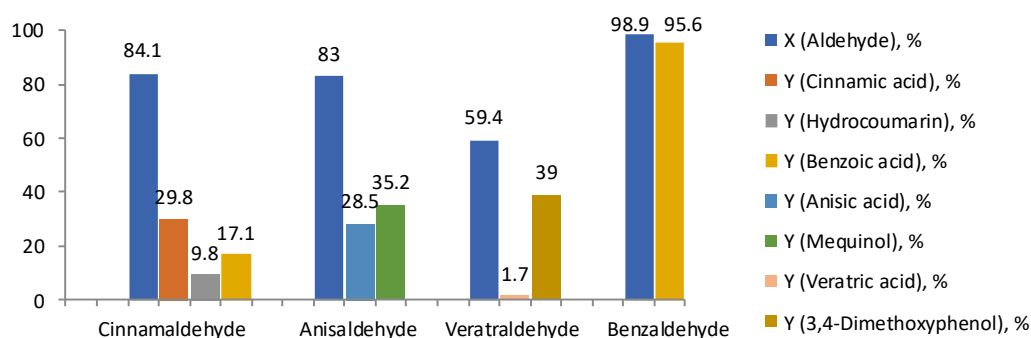


Fig. 5. Effect of catalyst activity on the oxidation reaction of a number of aromatic aldehydes. Toluene:water ratio=4:1. Reaction temperature – 50 °C. h. Reaction time – 8 h.

The reusability of the catalyst was explored after separating the microgel from the reaction medium through precipitation using hexane. The catalytic performance remained largely unchanged, with less than a 3% reduction in benzoic acid yield even after the third cycle (Fig. 6a). FT-IR spectra of the used microgel demonstrated its chemical stability, showing no structural changes after three catalytic cycles (Fig. 6b).

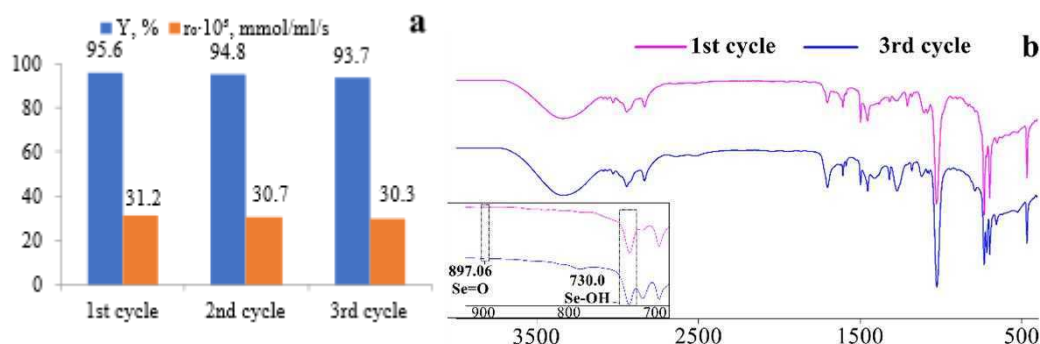


Fig. 6. a) Dependence of the benzoic acid yield (Y) and benzoic acid initial formation rate (r_0) on the reusability of the catalyst, solvent – toluene/water 4:1, catalyst – Se 2.0 microgel, reaction time – 8 h. b) FT-IR spectra of the microgel after first and third use of the catalyst in the oxidation reaction.

Conclusions

Se-containing microgel demonstrated high activity and selectivity as a low-temperature interfacial catalyst in the heterophase oxidation of benzaldehyde to benzoic acid by hydrogen peroxide. The highest yield of benzoic acid (95.6% with 96.6% selectivity) was achieved in the toluene/water (4:1) system at 50°C and 8 h reaction time. Reusing the catalyst over multiple cycles showed no significant change in its activity.

The catalyst also proved effective in the oxidation of other aromatic aldehydes, although with lower selectivity for the corresponding acids. High efficiency at the interface and mild working conditions make Se-microgel catalysts promising candidates for green oxidation processes using hydrogen peroxide as an environmentally safe oxidant.

Acknowledgments

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Tuning Excited-State Proton Transfer in 3-Hydroxyflavones by Inclusion Into β -Cyclodextrins

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Abstract. *By combining fluorescence titration with molecular docking, we discovered that dodecyl fatty acid-modified 3HF- $C_{11}COOH$ interacts strongly with β -cyclodextrin (β -CD). However, its insertion mode differs from that of unsubstituted 3HF. The β -CD-encapsulated 3HF- $C_{11}COOH$ adopts an unfavourable conformation for excited-state intramolecular proton transfer (ESIPT), as the intramolecular hydrogen bonding is partially disrupted.*

Keywords: flavonol, fluorescent probe, green chemistry, host-guest complex, ESIPT.

Introduction

Cyclodextrins (CDs) are cyclic oligosaccharides characterised by a hydrophobic inner cavity and a hydrophilic outer surface. This structure enables them to form host-guest complexes with various molecules, including natural and synthetic flavonols. Flavonols, such as robinetin, are plant-derived compounds known for their therapeutic properties and fluorescence [1]. Their ability to fluoresce makes them suitable probes for studying interactions within the cyclodextrin cavity. Some synthetic fluorescent flavonols are used to probe hydrophobic cyclodextrin cavities due to their unique properties that allow for effective interaction and encapsulation [1, 2]. When a flavonol is introduced to a cyclodextrin solution, it can enter the hydrophobic cavity, displacing water molecules and forming a stable inclusion complex [2, 3]. This process can be monitored through changes in fluorescence intensity, which provides insights into the binding dynamics and capacity of the cyclodextrin [3]. The use of fluorescent flavonols in cyclodextrin studies has applications in drug delivery systems, where the inclusion of therapeutic agents can enhance solubility and bioavailability [1, 4]. Additionally, these studies help in understanding molecular recognition processes and the design of better supramolecular systems. Various studies have investigated the inclusion of flavonols in cyclodextrin cavities, employing techniques such as steady-state and time-resolved fluorescence spectroscopy to analyse the binding interactions and thermodynamics involved.

Results and Discussion

The Excited State Intramolecular Proton Transfer (ESIPT) process in 3-hydroxyflavone (3HF) involves the transfer of a proton from the hydroxyl group to the carbonyl group upon photoexcitation [5, 6]. This transfer occurs in the excited state and is facilitated by the formation of a strong intramolecular hydrogen bond. ESIPT is highly effective in non-polar aprotic solvents; however, it can be hindered in polar protic solvents. In these solvents, the formation of competitive hydrogen bonds with the solvent can disrupt the tautomerism process [7, 8]. To enhance the fluorescence intensity of 3-hydroxyflavone in an aqueous medium, various supramolecular cages

can be used to create hydrophobic environments [2, 3]. Additionally, hydrophobic modifications of the parent 3-hydroxyflavone can help to enhance and fine-tune binding interactions [9-11].

To investigate the impact of introducing a fatty acid group at the C4' position of the terminal phenyl ring in the flavone structure, we synthesised a new derivative of 3-hydroxyflavone (3HF), termed 3HF-C₁₁COOH [11]. We then examined its binding interactions with β -CD and compared these findings to those of the parent unsubstituted 3HF (see Fig. 1).

Figure 1a illustrates how increasing the concentration of β -CD affects the emission behaviour of 3HF. It is evident that the addition of β -CDs induces significant changes in the emission characteristics. The weak fluorescence band at the shorter wavelength, measured at 395 nm, can be attributed to the normal (non-proton-transferred, N*) emission. In contrast, the intense fluorescence band at the longer wavelength of 517 nm corresponds to the emission from the ESIPT tautomer (T*) [7, 9]. These observations align well with previously reported studies [3]. As the concentration of β -CD increases, the intensities of both the normal N* and tautomeric T* forms of 3HF also increase. This notable enhancement in fluorescence suggests that 3HF is being incorporated into relatively hydrophobic environments, thereby minimizing the perturbation of the surrounding water environment.

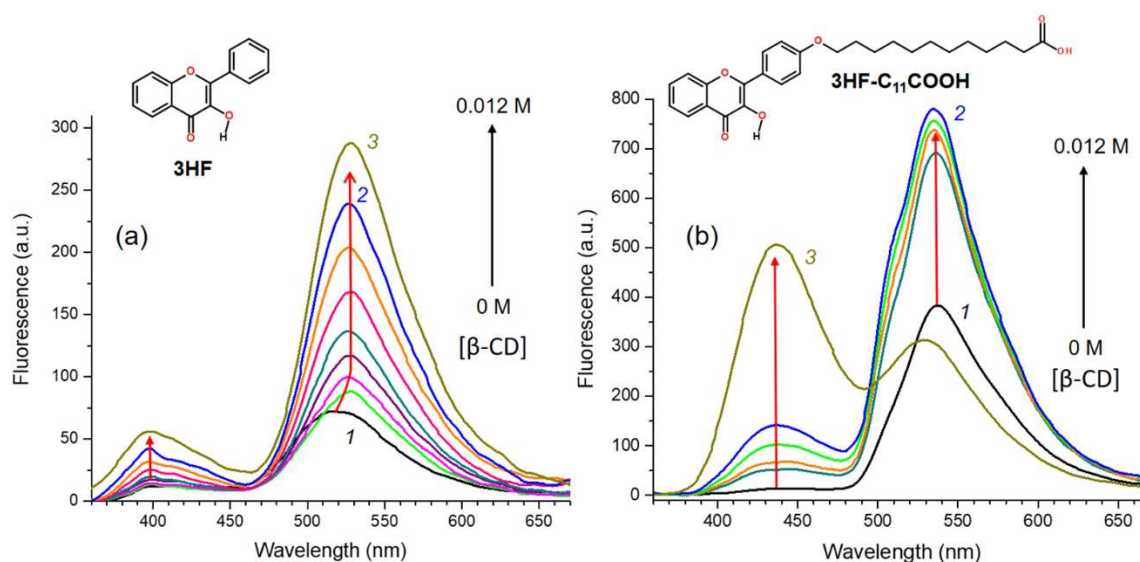


Fig. 1. Fluorescence titration of 3HF (a) and 3HF-C₁₁COOH (b) was conducted using β -CD in a phosphate buffer at pH 6.86. The concentrations of 3HF and 3HF-C₁₁COOH were 1.1×10^{-5} M and 1.3×10^{-5} M, respectively. The concentration range for β -CD is provided in the insets for the first 1 (no β -CD) and last titration spectra 2 (in the presence of 0.012 M β -CD). The spectrum 3 corresponds to the probe's fluorescence in concentrated β -CD stock. The red arrows indicate the increase in fluorescence upon the addition of β -CD.

Figure 1b illustrates the changes in emission behaviour of 3HF-C₁₁COOH upon the addition of β -CD. In a phosphate buffer, the fluorescence spectrum of 3HF-C₁₁COOH predominantly shows the tautomer emission at 537 nm. However, with the addition of β -CDs, the fluorescence intensity increases, accompanied by the emergence of a notable dual band, which includes a short-wavelength band at 435 nm. Interestingly, the ratio of normal to tautomeric bands (N*/T*) shifts further towards dominance of the N*-band when 3HF-C₁₁COOH is dissolved in concentrated β -CD stock solution, as depicted in Fig. 1b (spectrum 3). Moreover, this phenomenon was not observed for 3HF Fig. 1a (spectrum 3). So, these fluorescence changes suggest that some encapsulation of 3HF-C₁₁COOH within β -CD has occurred. However, the inserted conformation and interaction modes of 3HF-C₁₁COOH differ significantly from those of unsubstituted 3HF. The

appearance of the intense short-wavelength band N* indicates that the ESIPT process is no longer active in the encapsulated form of 3HF-C₁₁COOH. Several mechanisms may explain the reduction in T* intensity: (i) 3HF-C₁₁COOH may enter into β -CD in an unfavourable conformation that interrupts the intramolecular hydrogen bond between the 3-hydroxy group and the carbonyl oxygen; (ii) 3HF-C₁₁COOH may engage in competitive hydrogen bonding with solvent water molecules; (iii) 3HF-C₁₁COOH may form competitive hydrogen bonds with the primary or secondary hydroxyl groups of the β -CD macrocycle.

Numerous experimental and theoretical studies have focused on elucidating the molecular aspects of flavonol-host interactions. It has been proposed that cyclodextrins form inclusion complexes with flavonols through non-covalent interactions, in which the hydrophobic aromatic rings of flavonols are encapsulated within the cavity of the cyclodextrin [12]. This process stabilizes the flavonols against degradation (such as oxidation) and enhances their water solubility. In this context, β -CD is most widely used due to its cavity size, which can accommodate flavonols like hesperetin and naringenin, as it consists of seven glucose units. However, a recent MD simulation study revealed that several insertion modes of 3HF were possible with larger-sized γ -CD, in which 3HF was encapsulated by either the chromone ring or the phenyl ring, respectively [13].

To elucidate atomistic aspects of host-guest interactions, we carried out molecular semi-flexible docking calculations. Upon docking of 3HF and 3HF-C₁₁COOH with β -CD, the conformation of the host macrocycle was held fixed at the symmetrical cone conformation optimised at the B3LYP-cc-PVDZ level. The probe conformation was allowed to adapt upon docking. Molecular docking calculations were carried out by AutoDock Vina [14].

Fig. 2 illustrates the favourable insertion modes of 3HF and 3HF-C₁₁COOH estimated by molecular docking. It can be seen that 3HF inserts deep into the β -CD cavity (Fig. 2a). Such insertion mode can indeed shield the 3-hydroxy group from specific interactions with surrounding solvent molecules. In contrast, the presence of the bulky dodecyl fatty acid moiety alters the insertion mode of 3HF-C₁₁COOH, so that the 3-hydroxyflavone core is pushed away from the host cavity, as illustrated in Fig. 2b.

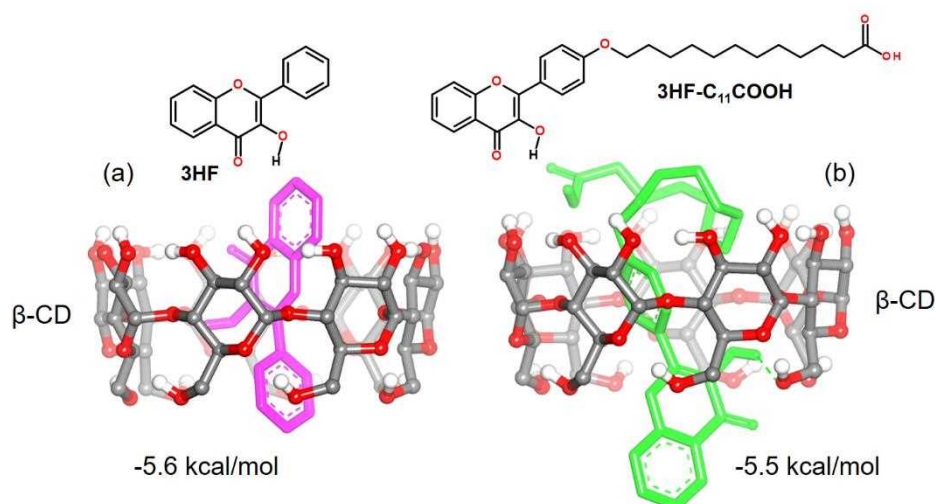


Fig. 2. Molecular docking of 3HF (a) and 3HF-C₁₁COOH (b) with β -CD.

The inspection of Fig. 2b reveals that the dodecyl carboxy group adopts a coil conformation and interacts with β -CD at the wider rim, which is composed of secondary hydroxyl groups. As a result, the flavone ring and the 3-hydroxy group fit into the narrow rim of β -CD. Importantly, molecular docking indicates that in this inserted conformation, the 3-hydroxy group forms an

intermolecular hydrogen bond with a primary hydroxyl group of β -CD. This interaction may disrupt the intramolecular hydrogen bonding that is responsible for the ESIPT process.

Molecular docking indicates that while the binding/insertion energy for both 3HF and 3HF- $C_{11}COOH$ is quite similar at -5.6 kcal/mol and -5.5 kcal/mol, respectively, the inserted conformations differ significantly in terms of protecting the essential ESIPT moiety within the hydrophobic β -CD host. The β -CD-encapsulated 3HF forms a rigid, water-protected structure. In contrast, the presence of the hydrophobic dodecyl fatty acid group competes with the 3-hydroxyflavone moiety for entrapment in the hydrophobic region of β -CD. This competition results in the encapsulation of 3HF- $C_{11}COOH$ in an ESIPT-unfavourable conformation, disrupting the intramolecular hydrogen bonding interactions that are favourable for intramolecular proton transfer.

Conclusions

The encapsulation of fluorescent flavonols into cyclodextrins (CDs) is a well-researched strategy to enhance their solubility, stability, and bioavailability [15]. Cyclodextrins, with their hydrophobic cavities and hydrophilic exteriors, form inclusion complexes with hydrophobic molecules like flavonols, improving their physicochemical properties [16, 17]. Therefore, improving the solubility of flavonols in non-toxic and easily available solvents like water allows us to address both research and practical challenges within green chemistry.

Our fluorescence titration experiments demonstrated that dodecyl fatty acid modified 3HF- $C_{11}COOH$ interacts strongly with β -CD. However, introducing a long alkyl chain at the C4' position of the terminal phenyl ring in the flavone structure alters its insertion mode compared to the unsubstituted 3HF. Molecular docking of both flavones also suggests that the inserted conformation and interaction modes of 3HF- $C_{11}COOH$ differ significantly from those of unsubstituted 3HF. The β -CD-encapsulated 3HF- $C_{11}COOH$ adopts a conformation that is unfavourable for ESIPT, where the intramolecular hydrogen bonding interactions that typically facilitate this process are partially disrupted. Our findings provide insights into the molecular aspects of flavone-host interactions, which enable the tuning of ESIPT in β -CD-encapsulated 3HF derivatives.

Acknowledgments

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Design of Polyfunctional Catalysts for C₂, C₄ (Bio)alcohols' Conversion Into Valuable Alkenes and Oxygenates

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Abstract. *The scientific approaches to a structural-functional design of effective catalysts for multi-stage processes of C₂, C₄ (bio)alcohols' conversion into industrially important compounds are considered. The research results of the catalysts for processes: ethanol → butan-1-ol → 2-ethylhexan-1-ol, ethanol → buta-1,3-diene, and isobutanol → butene isomers are analysed and summarized.*

Keywords: polyfunctional catalysts, (bio)alcohols' conversion, butenes, buta-1,3-diene, 2-ethylhexan-1-ol.

Introduction

The development of catalytic processes for C₂, and C₄ (bio)alcohols' conversion into industrially important hydrocarbons/oxygenates is becoming increasingly relevant, as it allows the production of fuel components and polymers from renewable raw materials. The availability of highly active/selective catalysts is the key condition for ensuring the competitiveness of such processes compared to the ones based on petroleum. Processes for the conversion of ethanol (EtOH) into butan-1-ol (1-ButOH), 2-ethylhexan-1-ol (2-et-HexOH), and buta-1,3-diene (1,3-BD), as well as the conversion of isobutanol (i-ButOH) into butene isomers, are multi-stage tandem processes, for the acceleration of which active sites of different natures are necessary.

A mechanism of alcohol condensation with carbon chain elongation is still under debate. However, most scientists agree on the following sequence: dehydrogenation of the initial alcohol to an aldehyde, aldol condensation, dehydration of the aldol product to an unsaturated aldehyde (crotonic condensation), hydrogenation and Meerwein-Ponndorf-Verley (MPV) reduction of the unsaturated aldehyde into a desired higher saturated alcohol or dehydration of the unsaturated alcohol to form a diene product [1]. Dehydrogenation of an initial alcohol and aldol-crotonic condensation are key stages of the processes of obtaining both a higher alcohol and a diene. The reported reaction rates correlate with redox and acid-base properties of a catalyst surface. As perspective heterogeneous catalysts with an opportunity to regulate functional (redox, acid-base) properties, Mg (Zr)-Al (Si) mixed oxides and hydroxyapatites (HAp) are considered.

The dehydration of i-ButOH into butene isomers is studied on acidic catalysts (oxides, zeolites). The growing interest in studying i-ButOH dehydration on zeolites is attributed to the achieved high (~80%) selectivity towards linear butenes (but-1-ene, *trans*-but-2-ene, and *cis*-but-2-ene) over FER-type zeolites at 225–275°C [2]. Acidic surface sites are necessary for both dehydration and isomerization, being key stages of the process of obtaining linear butenes from i-ButOH. The active site's nature, strength, and localization significantly affect the distribution of products. A thorough understanding of the effect of acid-base characteristics of different structure-

type zeolites on their catalytic properties will enable designing an effective catalyst for the i-ButOH conversion into linear butenes at moderate temperatures (175–225°C).

Given the foregoing, physicochemical principles of creating effective catalysts for C₂, and C₄ (bio)alcohols' conversion into industrially important compounds are presented, namely, ethanol → butan-1-ol → 2-ethylhexan-1-ol, ethanol → buta-1,3-diene, and isobutanol → butene isomers. The results obtained by our research group during the last decade are summarized.

Materials and Methods

HAp and Mg (Zr)-Al (Si) mixed oxides (including hydrotalcite-derived ones) modified by activated carbon, alkaline (Na, K), alkaline earth (Mg, Sr), rare-earth (REE: Y, La, Ce) and transition metals (W, Mo) are prepared for the conversion of EtOH and 1-ButOH. FER, MFI, FAU, and BEA zeolites (Si/M=10–200) with heteroelements (M = B, Al, Fe, Ga) are prepared for i-ButOH conversion. The samples are studied by SEM, XRD, N₂-ad(de)sorption, NMR, XPS, PIXE/RBS, EPR, FTIR-Py, and TPD-NH₃/CO₂.

Results and Discussion

Guerbet condensation of alcohols with subsequent carbon chain elongation could be implemented in batch and continuous flow reactors using homogeneous, heterogeneous, and combined homogeneous and heterogeneous catalytic systems. For the first time, a principal possibility of producing 2-et-HexOH via vapor-phase successive condensation of EtOH and 1-ButOH over Mg-Al oxide catalysts in a flow mode has been shown by our research group [3]. The challenge remains in developing a catalyst with high yield/selectivity towards C₅₊ alcohols. As stated above, regulating redox and acid-base characteristics of the catalysts for alcohol conversion into both a higher alcohol and a diene affects the process selectivity. To enhance functional (redox, acid-base) properties of the surface of HAp and Mg (Zr)-Al (Si) oxides, several strategies are considered: (i) non-equilibrium catalyst synthesis, (ii) dopant engineering, e.g., a modification by alkaline, alkaline earth, rare-earth, and transition metals, (iii) catalyst support engineering, in particular a modification by activated carbon.

The surface acid/base capacity ratio, caused by changing the Mg/Al ratio of Mg-Al-O-based systems, affects the target product's yield in EtOH conversion into 1-ButOH and higher C₅₊ alcohols (Table 1). Based on the study of Mg-Al-O-based systems with different times of hydrotalcite preparation, reducing the maturation time of the mother liquor after coprecipitation from 24 to 1 h is found to increase the volume and total surface area of mesopores, external area of the samples, and also the concentration of weak and medium-strength basic sites. These in turn increase the catalysts' activity and selectivity towards 1-ButOH during EtOH conversion [4]. An improvement in selectivity over Mg-Al-O catalysts is achieved using REE doping and, thus, the formation of acid-base sites, intensifying the key stage, namely, aldol condensation of acetaldehyde (AcH). The addition of Mo(W) compounds also leads to the enhancement of redox properties of the catalyst's surface and, therefore, boosts the EtOH dehydrogenation stage [5].

The effect of alkaline and alkaline earth metals is investigated for Zn-Mg(Zr)Si-O systems and HAp, respectively. The modification of Zn-MgSi oxide systems by Na⁺/K⁺ promotes an increase in the selectivity towards 1,3-BD during EtOH conversion (at ≥400°C) by reducing the number of sites responsible for by-product formation. For Zn-ZrSi oxide systems, alkali metal additives lead to a decrease in the ethene and diethyl ether (DEE) selectivity due to a decrease in the content of strong acidic sites that are active in the side EtOH dehydration reaction [6]. The partial replacement of Ca²⁺ ions by Mg²⁺ and Sr²⁺ in the HAp structure is found to cause both a decrease in the number and strength of basic sites on the surface and a redistribution of the strength

of acidic sites. The HAp catalysts show high activity (up to 57%) and selectivity up to 80% in vapor-phase condensation of both EtOH and 1-ButOH [7].

Table 1

Catalytic properties of Mg-Al-O systems in EtOH conversion at 275°C, 0.14 h⁻¹

Catalyst	Conv. (%)	ButOH + HexOH Sel. (%)	AcH Sel. (%)	Ethene + DEE Sel. (%)	Others Sel. (%)
Mg-Al (2:1)	30	75	4	4	17
Mg-Al (2:1)- fast	40	71	1	8	20
Mg-Al-Y (2:0,9:0,1)	20	84	3	8	5
Mg-Al-La (2:0,9:0,1)	20	57	18	10	15
Mg-Al-Ce (2:0,9:0,1)	14	74	3	9	14
Mg-Al (3:1)	28	74	7	5	14
Mg-Al (3:1)- fast	33	74	2	11	13
Mg-Al-Mo (3:0,9:0,1)	29	87	4	2	7
Mg-Al-W(3:0,9:0,1)	29	87	4	2	7

The development of active/selective catalysts for linear butenes from i-ButOH with high operation stability is a relevant task. The presence of a larger number of strong Brønsted acidic sites (with NH₃ desorption activation energy of ~ 125 kJ/mol) on the surface of Al-FER and Al-MFI zeolites is found to promote the formation of linear butenes with the 73 and 35% selectivity (Table 2). The predominance of strong Lewis acidic sites on the surface of Al-FAU and Al-BEA leads to the formation of by-products: isobutene, C₂-C₅₊ (un)saturated and aromatic hydrocarbons, and oxygen-containing compounds [8]. The acid-base characteristics can be modified by isomorphic substitution of Al in the zeolite framework both during synthesis and post-synthetically. The incorporation of Fe and Ga heteroelements in the MFI framework leads to an improved selectivity towards linear butenes [9]. On the MFI surface, the presence of acidic sites, formed with the participation of iron, ensures i-ButOH conversion into linear butenes with a 75% selectivity at 175°C, which exceeds those over Al-FER. MFI is characterized by a smaller water retention capacity, which can contribute to high operational stability over time.

Table 2

Catalytic properties of different structure-type zeolites in i-ButOH conversion at 175°C, 1 h⁻¹

Catalyst	Conv. (%)	Linear butenes Sel. (%)	Isobutene Sel. (%)	Others Sel. (%)
Al-FER	18	73	24	3
Al-MFI	30	35	57	8
Fe-MFI	39	75	21	5
Ga-MFI	23	62	35	3

Conclusions

In the L.V. Pisarzhevskii Institute of Physical Chemistry of the National Academy of Sciences of Ukraine (NASU), effective oxide catalysts for obtaining 1,3-BD and C₅₊ alcohols from EtOH are developed. For the first time, vapor-phase condensation of ButOH into 2-et-HexOH is realized in a flow mode over modified Mg-Al-O and HAp catalytic systems. The possibility of sequential transformation: EtOH → ButOH → 2-et-HexOH, under atmospheric pressure in a flow reactor is confirmed. This will allow obtaining 2-et-HexOH directly from EtOH. Effective under mild conditions (temperature of 175°C), iron silicate zeolite catalysts are developed, which ensure

i-ButOH conversion into linear butenes with selectivity at the level of known foreign analogs. This will create the prerequisites for establishing the production of strategically important polymer materials and motor-fuel components from renewable raw materials in Ukraine.

Acknowledgments

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Degradation Changes in the Crystal and Electronic Structure of Lead Iodide Perovskite

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Abstract. *The degradation of $\text{CH}_3\text{NH}_3\text{PbI}_3$ powder and films following exposure to air and X-ray radiation was investigated using X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and scanning electron microscopy. Our findings revealed significant differences in the states of PbI_2 and PbO between the films and the powder, as indicated by the energy positions of the Pb 4f and C 1s peaks. Additionally, a reduction in both the mass and size of the crystals suggests ongoing degradation processes.*

Keywords: Methylammonium Lead Iodide, electronic structure, crystal structure, degradation of perovskite, surface effects.

Introduction

Perovskites based on lead iodide have garnered significant attention due to their remarkable optoelectronic properties, which include a broad spectrum of light absorption from the near-infrared to the entire visible range, as well as a high absorption coefficient for incident radiation. The efficiency of solar cells utilizing perovskites has reached 26% [1], positioning them as a promising option for "green energy." Additionally, perovskite solar panels offer substantial advantages over traditional silicon panels: they are more cost-effective and simpler to manufacture. However, a considerable challenge to their widespread adoption is the material's inherent instability. Factors such as humidity, X-ray radiation, and heat [2] significantly impact this stability. Thus, when examining the properties of $\text{CH}_3\text{NH}_3\text{PbI}_3$, it is essential to consider specific conditions for a precise analysis.

This paper investigates the mechanisms of perovskite degradation under various influences, including air exposure, X-ray irradiation, electronic heating, and surface effects, all of which can profoundly affect research outcomes and practical applications.

Synthesis and Experiment

Samples of MAPbI_3 powder and films were synthesized through a well-defined process. For the powder synthesis, two solutions were prepared: lead iodide (PbI_2) in a 57% solution of hydroiodic acid and methylammonium iodide (MAI) in distilled water. The solutions were heated to 70°C and stirred, leading to the formation of crystals. After evaporation and washing, the final product consisted of black perovskite crystals. The synthesized powder was combined with dimethylsulfoxide (DMSO) to create perovskite films to form a viscous precursor solution. This solution was then dropped onto a glass substrate via centrifugation at 6000 rpm for 120 seconds.

Subsequently, the substrate with the applied paste was oven-baked at 80°C for 30 minutes to remove any residual DMSO.

X-ray diffraction studies were conducted at room temperature using a Shimadzu LabX diffractometer with CuK α radiation ($\lambda = 1.54178 \text{ \AA}$). The data was collected over a range of 2θ angles from 5° to 70°, with a step size of $\Delta(2\theta) = 0.02^\circ$. The “Match! 3” program, equipped with an open COD crystallographic database, was used to determine the phase composition of the samples.

X-ray photoelectron spectroscopy (XPS) was performed on the samples using a JEOL-Japan spectrometer with a magnesium anode (1253.6 eV). The spectra were calibrated to carbon at 284.8 eV.

Morphological analysis of the perovskite powder was carried out using scanning electron microscopy (SEM) on a Tescan Mira 3 microscope. The studied powder was adhered to carbon tape for imaging.

Results and discussion

The diffractogram of the synthesized methylammonium lead triiodide ($\text{CH}_3\text{NH}_3\text{PbI}_3$) is shown in Fig. 1. The positions and intensities of the reflections observed in the experimental diffractograms perfectly align with the corresponding peaks from the diffraction pattern of iodide perovskite available in the crystallographic database [3]. The relatively narrow diffraction peaks indicate a high degree of crystallinity in the organic-inorganic perovskite. The crystal size was determined from the peak at (220), which measures approximately 280 nm.

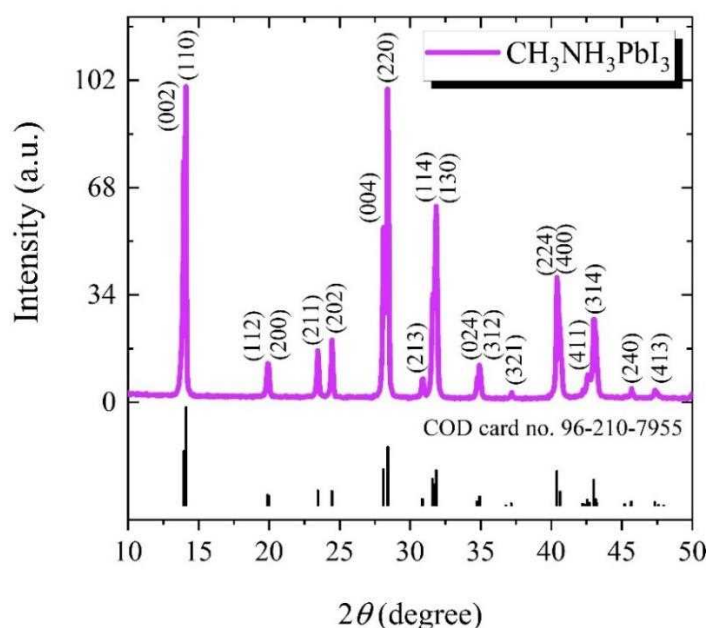


Fig. 1. Experimental diffraction pattern of lead iodide perovskite and a sample from the database of powder diffraction data (black lines).

Fig. 2 shows scanning electron microscope images of the powder, where, judging from image (a), the crystal size varies from 40-200 nm. Figures (b) and (c) show the degradation of the MAPbI_3 crystals, which is accompanied by the disintegration into small elongated crystallites, corresponding to the tetragonal structure of MAPbI_3 perovskite. The degradation begins with the drying of the crystal by iodine evaporation from the perovskite lattice (the beginning of the drying of the crystal is marked by a yellow circle in Fig. 2 b), and the release of PbI_2 onto the surface in the form of a hexagon (red circle in Fig. 2 c).

XPS spectrum of 4f – lead lines of MAPbI₃ powder is shown in Fig. 3. The spectrum is a 4f doublet of complex form with a splitting of 4.8 eV, and the positions of the centers of mass of the peaks -142.3 eV and 137.5 eV. Analysis of the spectra indicates the presence of lead Pb²⁺ in the octahedral environment of PbI₆ and PbO, which is a product of the decomposition of the synthesized sample.

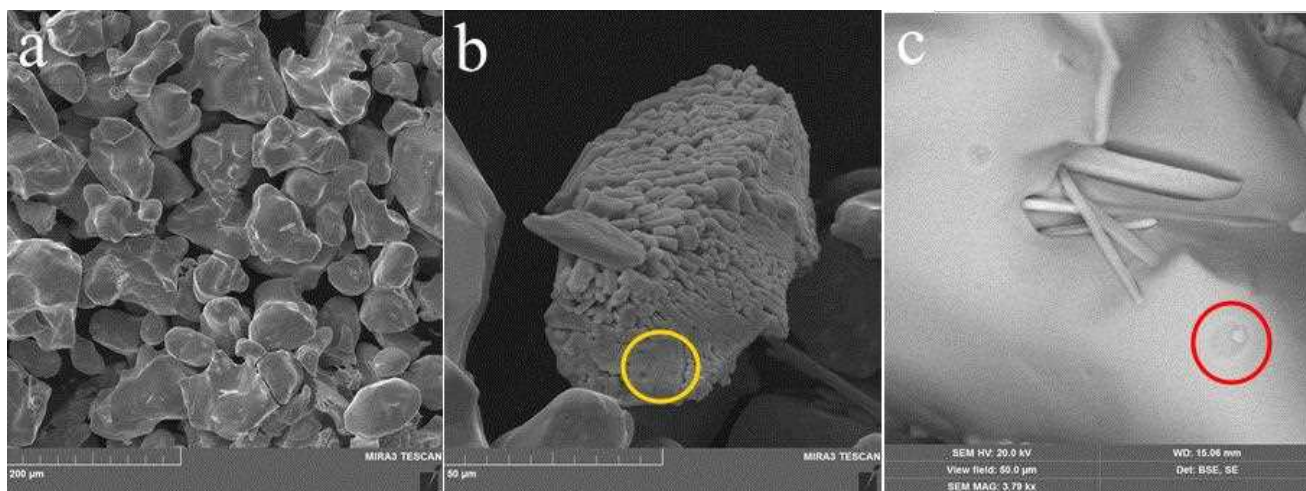


Fig. 2. SEM images of MAPbI₃ powder.

This indicates the beginning of perovskite degradation processes, which occur due to the high chemical activity and low ionization energy of iodine, which leads to the evaporation of a small amount of iodide and iodide [2]. Iodine ions are released from the lattice under the influence of X-ray irradiation, affecting the interaction with the organic cation CH₃NH₃⁺[2] Eq. (1):

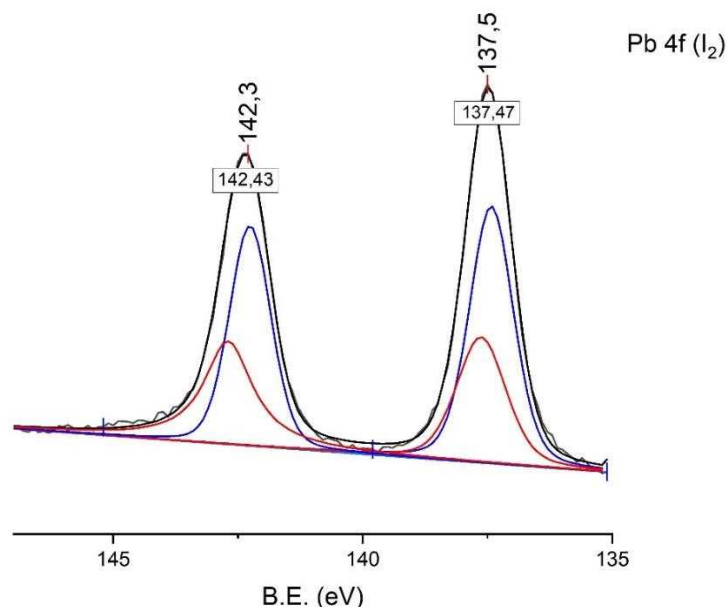
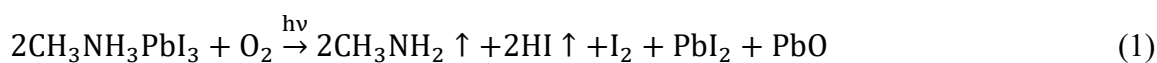


Fig. 3. X-ray photoelectron spectrum of Pb 4f of the compound CH₃NH₃PbI₃.

Figure 4 illustrates the core peaks of the Pb 4f(a) and C 1s(b) film sample at various exposure times throughout the day. The elevated position of the surface layers generally indicates a later contribution, which is associated with the presence of PbO [4]. This relationship is evident when the location is specified. Additionally, a minor chemical shift of 0.3 eV is observed, suggesting limited degradation of the Pb-I lattice in the peaks as exposure time increases.

The observed C 1s shift of 0.6 eV, as presented in Fig. 4b, likely indicates the presence of defects, such as iodine vacancies, or suggests that structural relaxation is occurring within the perovskite film [5].

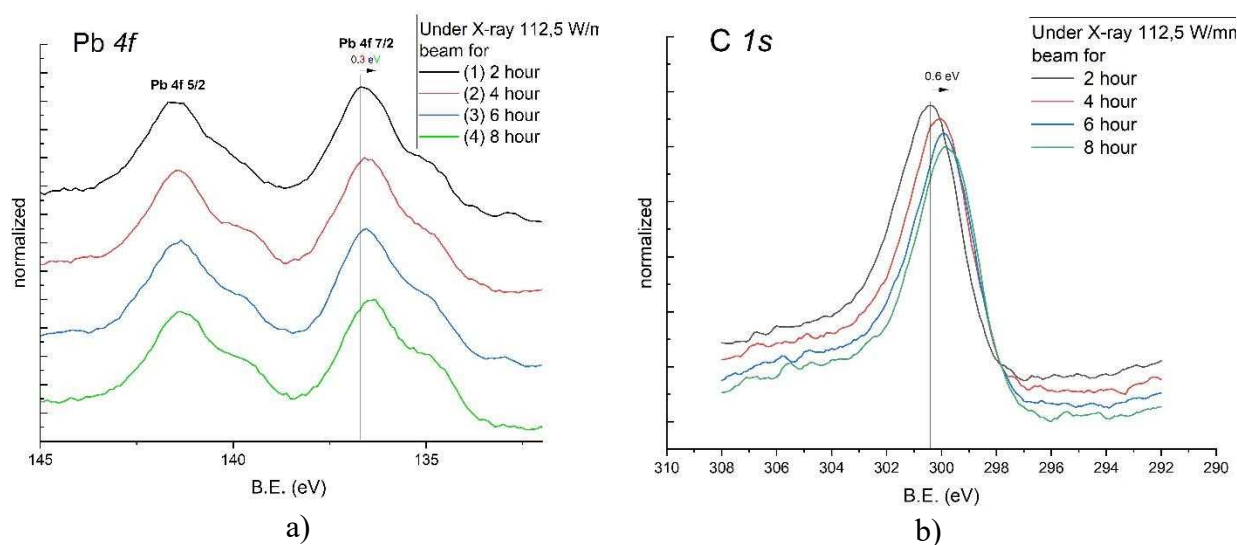


Fig. 4. XPS of MAPbI₃ film for 2-8 hours of exposure, (a) Pb 4f spectrum, (b) C 1s spectrum.

Conclusions

Structural studies reveal that the powder predominantly dries into elongated tetragonal crystals, with PbI₂ releasing onto the surface in a hexagonal form and a decrease in crystal size from 280 to 140 μm.

The application of X-ray irradiation accelerates the decomposition processes, influenced by the high chemical activity and low ionization energy of iodine. This results in the evaporation of some iodide and hydrogen iodide, altering the interaction between the organic cation CH₃NH₃⁺ and the crystal lattice.

An analysis of the electronic structure of both the powder and film indicates the presence of two distinct lead states: one corresponding to lead in the octahedral environment of PbI₆ and the other to lead in the PbO compound, a decomposition product of the original compound CH₃NH₃PbI₃. The perovskite film demonstrates a more pronounced alteration in the Pb states, likely due to its higher surface-to-volume ratio. Changes in the state of Pb may suggest a significant thermal reorientation of MA⁺, indicating a reduced interaction between the organic cation and the Pb-I lattice.

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Investigation of Suspensions of Mixed Iron Oxide/Manganese Oxide and Iron Oxide/Cobalt Oxide Nanoparticles in Aqueous Surfactant Solutions and Their Use for Mixer Studies in Liquids Feeds

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Abstract. *Mixed iron oxide/manganese oxide and iron oxide/cobalt oxide nanoparticles were synthesized by mixing ferrous chloride, ferric chloride, ammonium hydroxide, and manganese or cobalt chloride, followed by stirring, heating, and treatment with oleic acid. The size of magnetic nanotracers was analyzed using Nanoparticle Tracking Analysis (NTA) and used as magnetic markers for liquid feed mixing quality assessment.*

Keywords: stability of suspension, homogeneity of the feed mixing, magnetic nanotracers, nanoparticle tracking analysis, quality control.

Introduction

Ferromagnetic liquids (ferrofluids) are colloidal mixtures composed of nanoscale ferromagnetic particles suspended in a carrier fluid, usually an organic solvent or water. The ferromagnetic nanoparticles are coated with a surfactant to prevent their agglomeration (due to van der Waals forces and magnetic forces). The particles in a ferrofluid primarily consist of nanoparticles, which are suspended by Brownian motion and generally will not settle under normal conditions. Ferrofluids are used in such fields as vacuum rotating shaft seals, ink jet printers, electric wave absorbers, thermal energy converting materials, magneto-optical elements, etc.

Magnetite (Fe_3O_4) colloid is the main component of many ferrofluids. It is produced by two methods:

(1) a wet pulverizing method which comprises pulverizing a block of magnetite in a colloidal dispersion medium composed of a mixture of water and a surfactant in a ball mill for an extended period of time, and separating large particles to prepare a magnetic liquid [1];

(2) a wet precipitation method which comprises adding an alkali to a mixed aqueous solution of a ferrous salt and a ferric salt to co-precipitate fine particles of magnetite and thereafter peptizing them to prepare a magnetic liquid [2].

The advantage of the wet precipitation method utilizes the co-precipitation reaction of iron salts and leads to uniform nanosized particles of ferromagnetic oxides. It was easy to modify the composition of iron oxide-based ferromagnetic particles by the introduction of MnCl_2 , for example.

One of the potential applications of stable suspensions of $\text{Fe}_3\text{O}_4/\text{MnO}$ and $\text{Fe}_3\text{O}_4/\text{CoO}$ nanoparticles is the creation of nanotracers for the evaluation of mixer efficiency for liquid animal feed [3]. Creating a completely homogeneous mixture is a key stage in the production of both dry and liquid feeds. A statistical approach to the distribution of particles is often used to assess the quality of mixing of multicomponent dry compound feed [4,5]. This method assesses how well the ingredients are distributed in the mixture, ensuring that each portion of feed is uniform [6-8]. The reference [9] suggests several types of indicators that may be used as markers containing the

following information: a) designation of the type of crop, which refers to agricultural products; b) a specific feature related to an agricultural product; c) genetic content of an agricultural product.

In this study, we developed the methods for obtaining the ferromagnetic nanotracers $\text{Fe}_3\text{O}_4/\text{MnO}$ and $\text{Fe}_3\text{O}_4/\text{CoO}$ and demonstrated the capability of forming a stable suspension of the nanotracers in aqueous solutions of surfactants. The particle size of the nanotracer was determined using the NTA method, which relies on direct visualization and analysis of nanoparticles in aqueous media and includes two types of surfactants. The potential of using the prepared nanotracer to evaluate the quality of liquid feed mixing in laboratory conditions has been demonstrated.

Results and discussion

The following published procedure [3] was used for the preparation of $\text{Fe}_3\text{O}_4/\text{MnO}$ and $\text{Fe}_3\text{O}_4/\text{CoO}$ based ferrofluid. Into one liter of water 258 g of $\text{FeCl}_3 \times 6\text{H}_2\text{O}$, 86.8 g. of $\text{FeCl}_2 \times 4\text{H}_2\text{O}$ and 21.7 g of $\text{MnCl}_2 \times 4\text{H}_2\text{O}$ were dissolved with stirring by a glass rod (nonmagnetic). Separately 350 milliliters of ammonia was diluted into 350 ml of water, and then over a span of 75 seconds added to the iron salt solution. With continued stirring and heating, the colloidal magnetite was brought to 90 °C. Separately, 40 ml of oleic acid was added to 460 ml of heptane and added to the ammoniacal magnetite. After stirring the mixture for 15 minutes, the upper organic layer was drawn off. A stable ferrofluid results with a density of 1.032 g/ml and an apparent levitating density of 4.36 g/ml.

Preparation of $\text{Fe}_3\text{O}_4/\text{CoO}$ based ferrofluid was performed in similar manner with the following ratio between $\text{FeCl}_3 \times 6\text{H}_2\text{O}$, $\text{FeCl}_2 \times 4\text{H}_2\text{O}$ and $\text{CoCl}_2 \times 6\text{H}_2\text{O}$: (258: 82.3: 26.2 (w/w)).

In the next step, ferrofluid is dispersed into a 0.5% aqueous solution of surfactant: ammonium oleate or dimethylamine salt of oleic acid (DMAOA) at a ratio of ferrofluid: surfactant solution from 1:100 to 4:100 (w/w). After filtration through the Whatman 5 micron pore size filter paper, the stable suspension has been used for the determination of particle size distribution and colorimetric determination of manganese or cobalt content in the nanoparticles.

Nanoparticle Tracking Analysis is an innovative method for real-time observation and evaluation of nanoparticles in a liquid medium [10]. It utilizes laser microscopy to analyze Brownian motion via a CCD camera, with each particle tracked by a specialized image analysis program. NTA measures particle size and scattering intensity, enabling differentiation of heterogeneous nanoparticle mixtures and direct concentration determination. The resulting size distribution profile is presented as a number/frequency characteristic.

A focused laser beam refracts at the interface of a prismatic optical plate and the liquid layer above it, creating an illuminated region where nanoparticles become visible through a long-working-distance (x20) microscope objective. The NTA software detects and tracks each particle's movement, automatically calculating its displacement along the x and y axes.

Based on this data, the particle diffusion coefficient (D_t) is calculated. Knowing the sample temperature and the solvent viscosity, it is possible to determine D_t :

$$D_t = k_B \times T / (3\pi\mu d_h), \quad (1)$$

where k_B is the Boltzmann constant, μ is the viscosity coefficient. The hydrodynamic diameter (d_h) is determined using the Stokes-Einstein equation [11].

To obtain a statistically reliable and reproducible particle size distribution in an acceptable time frame (e.g., less than 60 seconds), the particle concentration in the sample should be between 10^7 and 10^9 particles per milliliter. If necessary, the sample is diluted to the desired concentration.

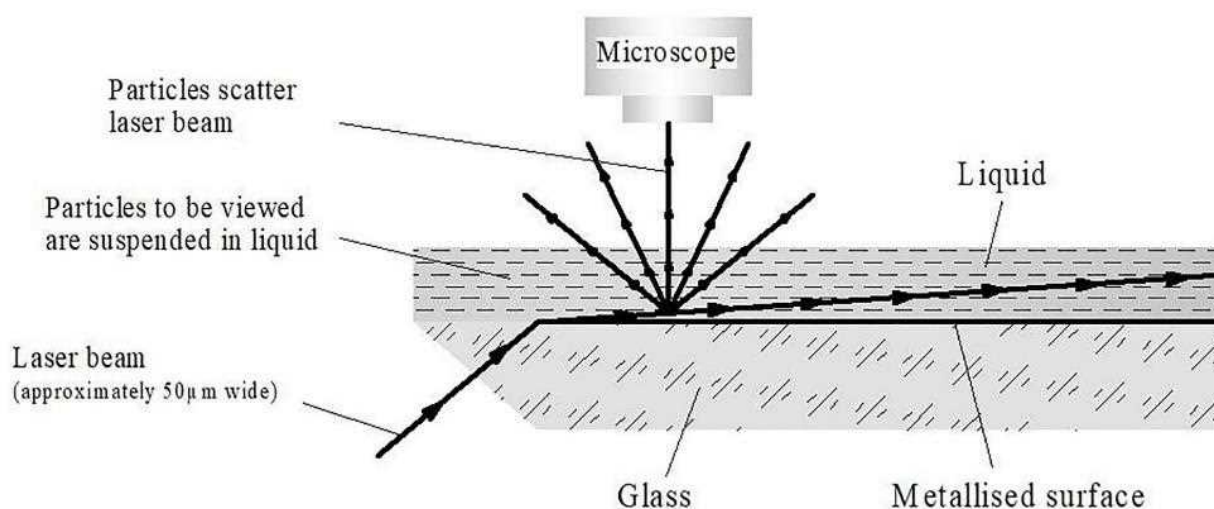


Fig.1 . Methodology of the NTA method.

An example of a particle size distribution in suspension of $\text{Fe}_3\text{O}_4/\text{MnO}$ nanoparticles in solutions with two different surfactants is shown in Table 1.

Table 1

Particle size distribution in the suspension of $\text{Fe}_3\text{O}_4/\text{MnO}$ nanoparticles

D values*	Sample A (0.5% solution of DMAOA)		Sample B (0.5% solution of ammonium oleate)	
	Reported	Normalized to 100%	Reported	Normalized to 100%
D10	44	13.5	71	12.7
D50	73	22.3	124	22.3
D90	119	36.4	203	36.4
D70	91	27.8	159	28.6
Total amount of analyzed particles	327		557	

*D10, D50, D70, and D90 are the mean sizes of particles below 10, 50, 70, and 90 nm, respectively.

Potential applications of prepared stable suspension of ferromagnetic $\text{Fe}_3\text{O}_4/\text{MnO}$ and $\text{Fe}_3\text{O}_4/\text{CoO}$ nanoparticles are related to validating mixing of liquid feeds, as well as coding liquid additives, such as enzymes, and evaluation of their distribution in premixes and final feeds. Nanoparticles as components of magnetically retrievable liquid marker (tracer) have been tested in laboratory and production trials. The laboratory trial with an addition of liquid tracer (mixable with liquid enzyme added at concentration 110 ppm to the feed) at level 100 ppm to the dry feed, followed by retrieving the ferromagnetic nanoparticles and analyzing the content of manganese oxide and cobalt oxide in them yields 78% and 75% tracer recovery, respectively.

Conclusions

1. A method for making ferromagnetic iron oxide/manganese oxide and iron oxide/cobalt oxide nanoparticles has been developed, and their stability in aqueous solutions of surfactants has been evaluated.

2. The possibility of using a prepared stable suspension of ferromagnetic nanoparticles for validating the mixing of liquid feeds has been demonstrated.

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Catalytic Properties of CeO₂ and Its Nanocomposites with SBA-15 Mesoporous Molecular Sieve in Cyclic Carbamates Production from CO₂ and Aminoalcohols

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Abstract. *A series of CeO₂ materials and their composites with SBA-15 were obtained by decomposition of cerium ammonium nitrate at different temperatures and tested as catalysts for cyclic carbonates production from CO₂ and aminoalcohols. It was shown that reducing the decomposition temperature of cerium dioxide precursor from 500 to 300°C led to an increase in the conversion of 2-aminoethan-1-ol in the process of obtaining 1,3-oxazolidin-2-one under carbon dioxide pressure from 14 to 84%, which can be explained by an increase in defects with Ce³⁺ while for CeO₂/SBA-15 composites are inactive due to the adsorption of 2-aminoethan-1-ol on silanol groups of the surface and the absence Ce³⁺ particles in formed composites.*

Keywords: CeO₂, SBA-15, cyclic carbamate, carbon dioxide, composites, catalytic properties.

Introduction

Carbon dioxide (CO₂) is becoming increasingly important in global warming and climate change [1]. The amount of CO₂ in the atmosphere is increasing at an accelerated rate year by year. However, carbon dioxide is not only a greenhouse gas, but also a huge resource in the chemical industry. Carbon dioxide is a cheap, harmless, and non-flammable source of carbon. The direct synthesis of chemicals has attracted considerable attention. [2] However, due to the inert nature of CO₂, the range of possible conversion processes is limited. Therefore, it is crucial and urgent to develop efficient catalytic processes for converting CO₂ with minimal energy consumption.

Cyclic carbamates are a class of organic compounds which was widely used as monomers to produce polyurethanes and insecticides. Structural fragments of cyclic carbamates were part of antibiotics, in particular, linezolid and tedizolid [3]. Traditionally, highly toxic compounds such as phosgene, diphosgene, triphosgene, and substituted aziridines have been used to produce cyclic carbamates and carbonates [4]. However, these processes have significant drawbacks, namely the large number of by-products and the formation of toxic waste. The development of new catalysts for the safe production of cyclic carbamates is a promising direction for investigation.

Due to its pronounced acid-base and redox properties, CeO₂ has recently attracted much attention as a catalyst for organic synthesis. CeO₂-based materials were capable of catalyzing a wide range of reactions, in particular, the addition of carbon dioxide to aminoalcohols [5], alkenes (in the presence of a mild oxidant) [6], epoxides [7], with the formation of the corresponding cyclic

carbamates and carbonates. Various side reactions could occur due to the high pressure and temperature of the reaction.

The development of CeO_2 -containing catalysts that would increase the selectivity and conversion of the transformation into the corresponding products is a promising area of research. In this work, we investigated a series of Ce-containing materials, including composites.

Experimental

Synthesis of nanosized CeO_2 . 3.19 g of $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$ was placed in a muffle furnace and heated to the appropriate temperature (200 °C - 500 °C) for 2 hours [8]. After that, the samples were cooled to room temperature. Nanocomposites were obtained by impregnating the matrices of SBA-15 with a saturated solution of cerium ammonium nitrate with subsequent drying at a temperature of 100 °C and calcination at temperatures of 200 °C - 500 °C for 2 hours. SBA-15 was obtained according to the method described in detail in [9].

The synthesized CeO_2 samples were investigated as catalysts in the reactions of cyclic carbonates under excess pressure CO_2 using RVD-2-250 autoclaves (Riva Stal) with Teflon beakers. 2-ethanolamine, 2-amino-2-phenylethan-1-ol, and 2-amino-1-phenylethan-1-ol were used as starting alcohols. Methanol, ethanol, isopropanol, and acetonitrile were used as solvents. 100 equivalents of solvent, 1 equivalent of aminoalcohol, and 0.1 equivalent of CeO_2 were added to the autoclave. The autoclave was closed, purged with argon three times. CO_2 was introduced to a pressure of 50 atm. The RS was heated to 150 °C for an hour (the CO_2 pressure increased to 100 atm) and stirred at the specified temperature for 15 hours, after which the autoclave was cooled, and the pressure was reduced to atmospheric. The reaction mixture was investigated using NMR spectroscopy and gas chromatography.

Results and discussion

Fig. 1 shows the diffraction patterns of cerium oxide samples obtained by decomposition of cerium ammonium nitrate (Fig. 1, a) and its composites with SBA-15 (Fig. 1, b).

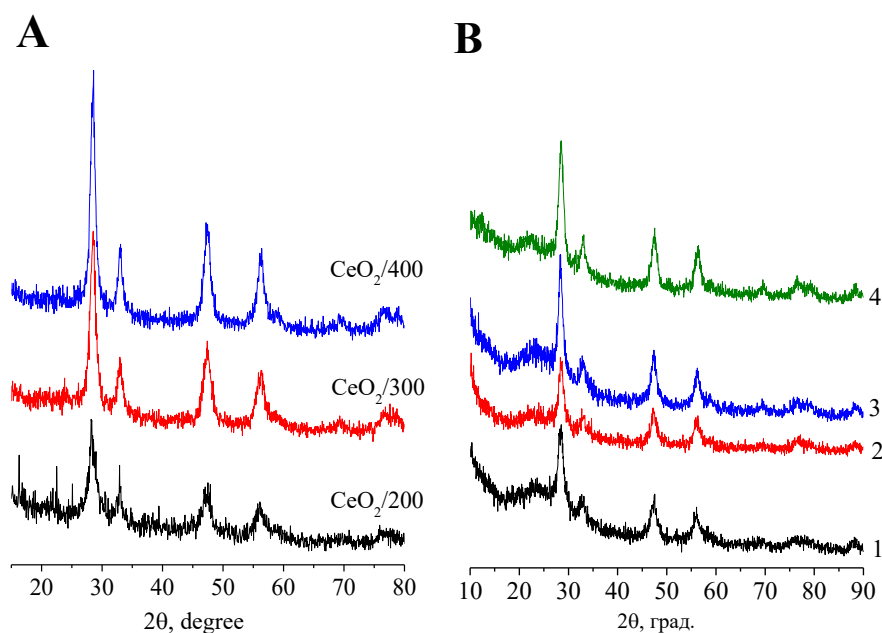


Fig. 1. Diffraction patterns of cerium oxide obtained by decomposition of cerium ammonium nitrate (A) and its composites with SBA-15 (B). Sample designations 1 - CeO_2 -SBA-15/200, 2 - CeO_2 -SBA-15/300, 3 - CeO_2 -SBA-15/400, 4 - CeO_2 -SBA-15/500.

All samples are characterized by the formation of crystalline cerium dioxide, which is the dominant crystalline phase. XRD pattern of the CeO₂/200 sample contained reflexes indicating the presence of incompletely decomposed cerium ammonium nitrate. The reflexes corresponding to cerium dioxide are broadened compared to the “bulk” analogue, which could indicate the formation of smaller particles compared to “ordinary” cerium dioxide.

The diffuse reflectance UV and visible electron spectra of cerium oxide prepared by decomposition of cerium ammonium nitrate at different temperatures are shown in Fig. 2. Absorption bands at approximately 235, 273, and 359 nm are observed for all CeO₂ samples [10]. The maxima at 273 and 358 nm can be attributed to electronic transitions from the valence band to the conduction band (O_(2p) to Ce_(4f)) and interband transitions, respectively. The maximum at 235 nm is most likely due to Ce³⁺ ← O²⁻ charge transfer [10]. For CeO₂-SBA-15, peaks at 220 and 290 nm were observed (Fig. 2a). These peaks could be attributed to Ce⁴⁺ ions in the formed composites. So that, in contrast to CeO₂ composites, CeO₂-SBA-15 contains only Ce⁴⁺ in its structure.

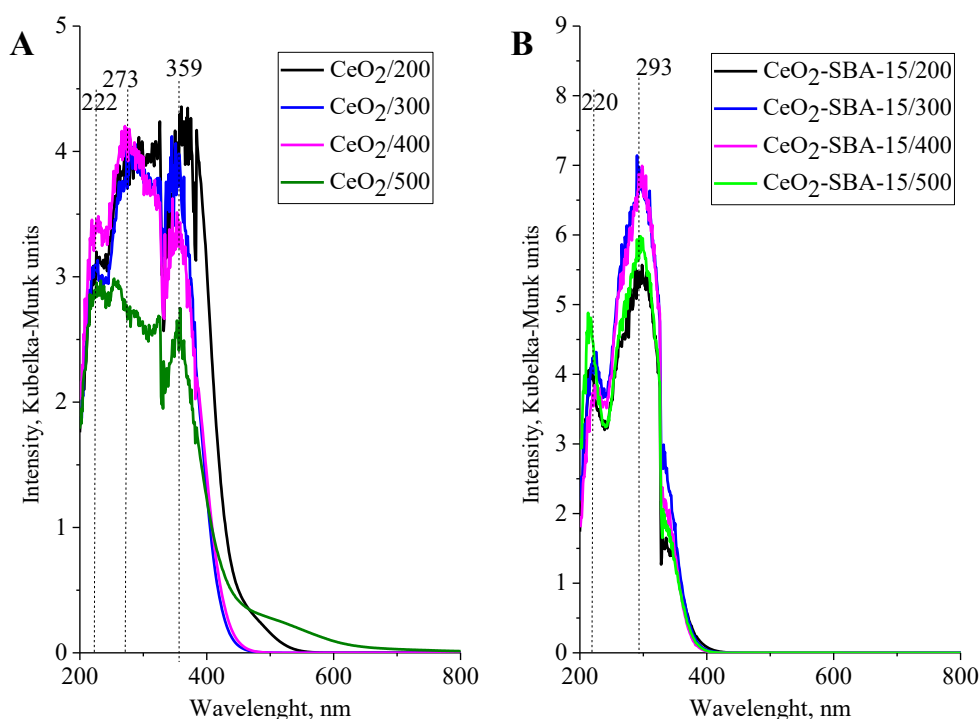


Fig. 2. DRUV spectra of CeO₂ (A) and CeO₂-SBA-15 (B) samples.

Catalytic properties of Ce-containing materials in the reaction of cyclic carbonate production from aminoalcohols and CO₂

A reaction scheme of the studied catalytic reaction of 1,3-oxazolidin-2-one (2-oxazolidinone) production from 2-aminoethanol in the presence excess of carbon dioxide is listed in Fig. 3.

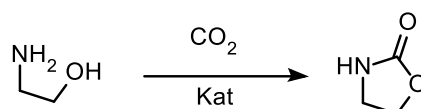


Fig.3. Reaction scheme for the conversion of 1,3-oxazolidin-2-one from 2-aminoethanol.

Data of catalytic Fig. 4 shows catalytic activity of CeO₂ and its composites with SBA-15. The highest yield of the 1,3-oxazolidin-2-one was achieved for the CeO₂/300 sample. For the samples CeO₂/400 and CeO₂/500 (decomposition temperatures above 300 °C) conversion of 2-aminoethanol decreased from 88 to 76 and 14%, respectively, which could be explained by a

decrease in the number of defects in the formed CeO_2 (a.b. at 357 nm. Fig 2.a), on which the catalytic process occurs. $\text{CeO}_2/\text{SBA-15}$ samples were inactive in this process due to the presence of silanol groups on which 2-aminoethanol adsorbed.

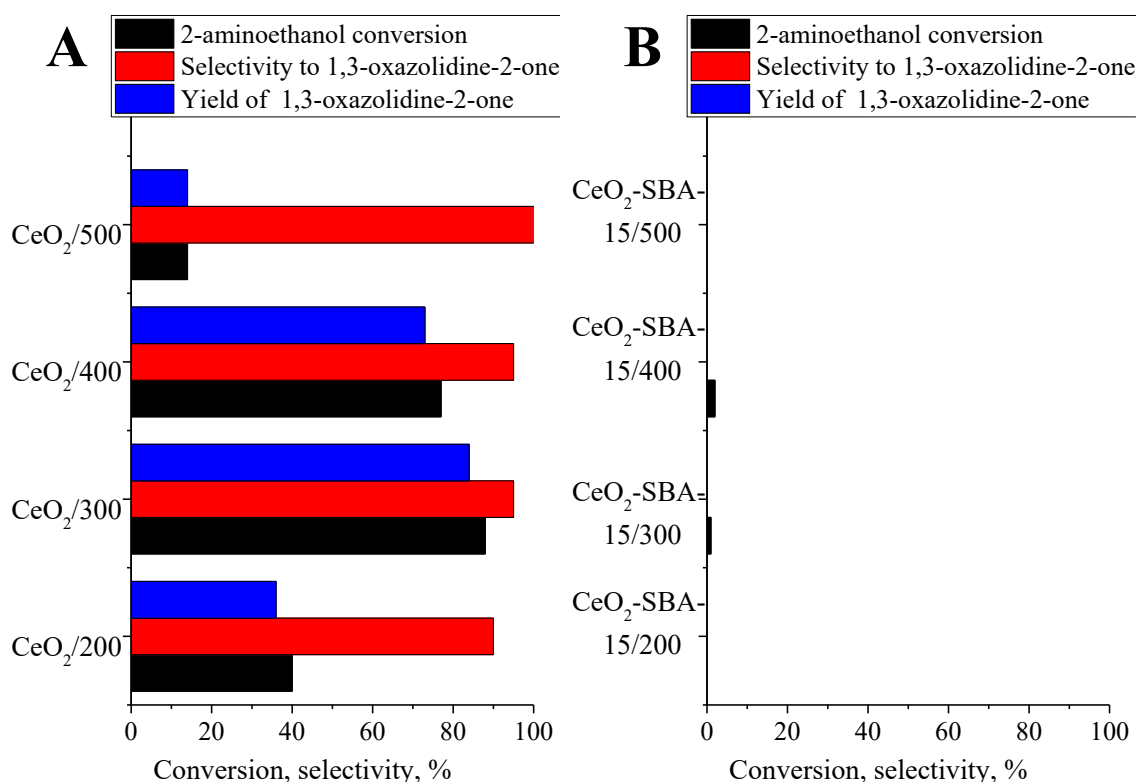


Fig.4. Catalytic activity of CeO_2 (A) and $\text{CeO}_2/\text{SBA-15}$ (B) in the process of 1,3-oxazolidin-2-one (2-oxazolidinone) production from 2-aminoethanol.

Depending on the solvent, the structure of the reaction by-product changed. In the case of isopropanol as a solvent, no by-products were detected (selectivity 100%), but the conversion of 2-aminoethanol was low (11%). The low yield in the case of using acetonitrile can be explained by the fact that aminoethanol forms aminoethanol hydrocarbonate from CO_2 , which was not soluble in the solvent and was removed from the reaction medium. The highest yield (62%) of the target product was obtained using methanol as a solvent.

Fig. 5 shows the catalytic properties of $\text{CeO}_2/300$ in the processes of obtaining cyclic carbamates from different structures. In the case of 2-aminoethanol, a significantly higher yield is achieved in this process compared to 2-amino-2-phenylethane-1-ol and 2-amino-1-phenylethane-1-ol. However, in the case of isomeric phenylaminoethanols, no reaction by-products were formed.

Conclusions

It is shown that the obtained materials based on CeO_2 are effective catalysts for the liquid-phase process of obtaining cyclic carbamates from carbon dioxide and aminoalcohols. For example, for the process of obtaining 1,3-oxazolidin-2-one, the highest yield of the target products was achieved at 84% for $\text{CeO}_2/300$. Changing the temperature of the precursor decomposition of cerium dioxide (cerium ammonium nitrate) from 500 to 300°C led to an increase in the conversion of 2-aminoethanol from 14 to 84%, which can be explained by an increase in defects with Ce^{3+} in the catalyst structure. $\text{CeO}_2\text{-SBA-15}$ composites are inactive in the process of obtaining 2-oxazolidinone from carbon dioxide and monoethanolamine, which may be due to the adsorption of monoethanolamine on silanol groups of the surface and the absence of Ce^{3+} in the formed composites.

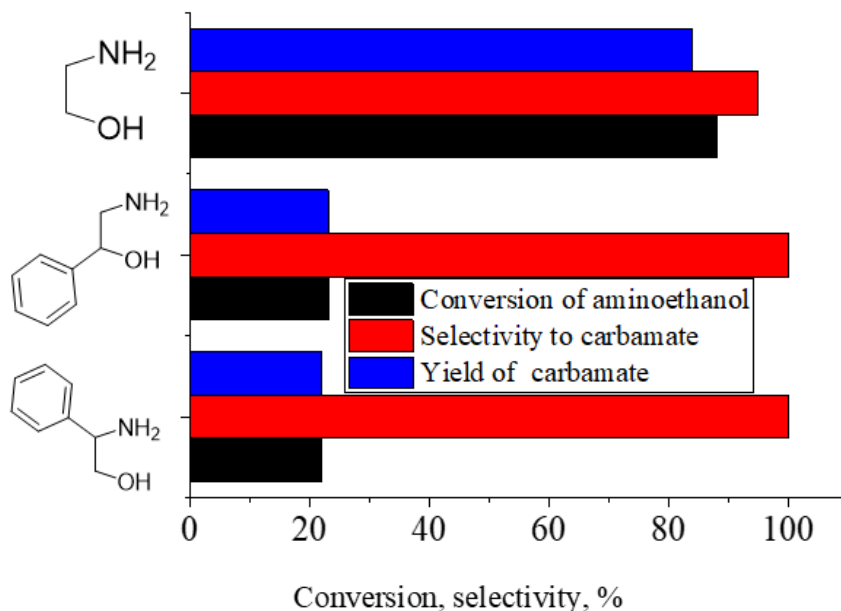


Fig.5. Catalytic properties of CeO₂/300 in the reaction of formation of cyclic carbamates from aminoalcohols using various substrates.

Acknowledgments

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Research on the Cracking of Heavy Oil Fractions Activated by Atmospheric Oxygen

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Abstract. *The study investigates the effectiveness of using atmospheric oxygen as an activator in the thermal cracking process under varying temperature conditions. It has been established that activation of thermal cracking significantly reduces the viscosity of the heavy residue, increases the yield of light fractions, and enhances the performance of the reaction system.*

Keywords: thermal cracking, vacuum residue, visbreaking, activator.

Introduction

The implementation of thermo-catalytic and hydroprocessing technologies for the upgrading of heavy petroleum residues is hindered by their high cost, capital intensity, and energy consumption. In contrast, thermal conversion processes for heavy residues are characterized by comparatively low capital and operational expenditures. However, their principal drawback is the relatively low yield of light hydrocarbon fractions (gasoline and diesel fuel), which typically does not exceed 20–40%.

Visbreaking is a process for upgrading heavy residues that, due to its relative simplicity in terms of technological and equipment design, enables the production of additional quantities of light petroleum products and marketable boiler fuels without the necessity for diluents. The integration of visbreaking units into refinery schemes is particularly relevant in the context of processing heavier crude oils or low-quality residues, as well as increasing demand for distillate products. Therefore, the development of methods for activating thermal conversion processes to enhance their efficiency and the yield of fuel fractions, while simultaneously obtaining commercially valuable residual products, represents a timely and important task [1].

Results and their discussion

The objective of the conducted experiments was to investigate the influence of temperature and the amount of activator (airborne oxygen) on the yield and composition of light hydrocarbon fractions, as well as to assess the feasibility of obtaining boiler fuel as a heavy residue that meets regulatory standards.

All experiments were conducted at atmospheric pressure and temperatures ranging from 420 to 440 °C. At the same time, the temperature of the cracking product vapors withdrawn from the reactor was maintained within the range of 310–320 °C.

To evaluate the efficiency of both activated and non-activated cracking processes, the following output parameters were used:

- Volumetric yield of light fractions (Vlf, vol.%) – defined as the ratio of the volume of the obtained light fraction to the total volume of the vacuum residue (asphaltenic feedstock) introduced into the process.

- Rate of light fraction formation (Wlf, vol.%/min) – the ratio of the change in the volumetric yield of the light fraction (ΔVlf) to the time interval ($\Delta \tau_p$) during which this fraction was collected.

In this study, light fractions were defined as all cracking products boiling at atmospheric pressure at temperatures not exceeding 360 °C. The volumetric yield of light fractions was used solely for the assessment of the cracking rate.

At this stage of the study, the dependence of the rate of light fraction formation on their volumetric yield was determined at three fixed temperatures (420, 430, and 440 °C), under a constant volumetric air feed rate, normalised per unit mass of vacuum residue loaded into the reactor. For the experiments presented, this rate was 3.0 L/(kg·min), corresponding to an actual air flow rate of 0.75 L/min.

Vacuum residue (gudron) derived from Western Ukrainian paraffinic crude oils was used as the feedstock for oxidised petroleum bitumen production.. The characteristics of the initial feedstock were as follows:

- Softening point (Ring-and-Ball method): 42 °C
- Ductility at 25 °C: 13 cm
- Penetration at 25 °C: 245 × 0.1 mm

Group composition (wt.%): - asphaltenes – 19.60; - resins – 24.38; - oils – 56.02; including paraffins – 5.42.

Table 1

Results of the study on the thermal cracking process of vacuum residue with and without air injection at a temperature of 420 °C

τ_p , min	Without air		With air: 3.0 l/(kg·min)	
	Vlf, vol.%	Wlf, vol.%/min	Vlf, vol.%	Wlf, vol.%/min
10	5.15	0.47	4.62	0.43
20	11.76	0.57	11.03	0.62
30	16.59	0.59	17.43	0.67
40	22.16	0.54	23.49	0.60
50	26.25	0.46	28.53	0.46
60	30.03	0.35	32.00	0.38
70	33.29	0.29	35.07	0.32
80	36.23	0.25	37.38	0.27
90	37.80	0.23	39.52	0.22

Table 2

Results of the study on the thermal cracking process of vacuum residue with and without air injection at a temperature of 430°C

τ_p , min	Without air		With air:3.0 l/(kg·min)	
	Vlf, vol.%	Wlf, vol.%/min	Vlf, vol.%	Wlf, vol.%/min
5	6.90	0.69	3.68	0.66
10	11.52	1.04	10.50	1.40
15	16.62	1.13	20.06	1.91
20	22.08	1.18	29.30	1.85
25	28.26	1.16	35.60	1.23
30	33.04	1.00	39.64	0.91
35	36.80	0.84	42.35	0.70
40	40.01	0.70	45.06	0.48

Based on the obtained dependencies, it can be concluded that the introduction of oxygen into the reaction mixture at the temperatures corresponding to active cracking of vacuum residue significantly increases the rate of light fraction formation compared to non-activated thermal cracking.

Table 3

Results of the study on the thermal cracking process of vacuum residue with and without air injection at a temperature of 440 °C

τ_p , min	Without air		With air: 3.0 l/(kg·min)	
	Vlf, vol. %	Wlf, vol. %/min	Vlf, vol. %	Wlf, vol. %/min
5	11.55	2.31	12.50	2.50
7	-	-	20.79	4.15
10	25.20	2.73	31.08	3.43
12	-	-	37.38	3.15
15	35.18	2.03	44.42	2.44
20	42.00	1.37	-	-

In particular, at a temperature of 420 °C, the rate of light fraction formation in the presence of oxygen activation increases by 10–15% (i.e., by a factor of 1.1–1.15) compared to conventional thermal cracking, with the reaction duration reaching approximately 100 minutes. When the temperature is raised to 430 °C, the rate increases by 30–40% (1.3–1.4 times), and the reaction time is reduced to 25–30 minutes. At 440 °C, the rate of formation rises by 50–60% (1.5–1.6 times), and the reaction is completed within 10–15 minutes.

Thus, the most pronounced effect of cracking rate enhancement is achieved at elevated temperatures, with the maximum reaction rate being realized within a shorter time interval from the beginning of the process.

To determine the optimal amount of activator—specifically, oxygen from air—a second series of experiments was conducted. In this series, the air feed rate into the reactor was varied from 0.5 to 1.0 L/min, corresponding to an equivalent volumetric flow rate of 2.0–4.0 L/(kg·min), at a constant temperature of 440 °C. The results are presented in Table 4.

Table 4

Results of the study on the thermal cracking process of vacuum residue with and without air injection at a temperature of 440 °C.

τ_p , min.	Without air		With air					
			2.0 l/(kg·min)		3.0 l/(kg·min)		4.0 l/(kg·min)	
	Vlf, vol. %	Wlf, vol. %/min	Vlf, vol. %	Wlf, vol. %/min	Vlf, vol. %	Wlf, vol. %/min	Vlf, vol. %	Wlf, vol. %/min
2	2.94	1.47	3.36	1.68	4.20	2.10	2.10	1.05
4	6.30	1.68	6.72	1.68	9.14	2.52	7.98	2.94
6	10.50	2.10	11.34	2.31	16.59	3.78	19.43	5.67
8	16.07	2.84	17.12	2.94	24.47	3.99	30.35	5.46
10	21.53	2.73	23.00	2.94	31.08	3.36	37.07	3.36

The data analysis showed that with an increase in the amount of air supplied over the same cracking time, the yield of light fractions increases by 15% in absolute terms (or more than 70% in relative terms). The activating effect of the oxygen in the air becomes even more evident when considering the dependence of the light fraction yield rate over time at varying air supply rates, which is observed as an increase in the light fraction yield rate by more than twice compared to cracking without air supply. The research results indicate that during the initial stage of the process (up to 6–8 minutes), the yield rate increases, after which it begins to decrease. This suggests a

decrease in the cracking reaction rate relative to polymerisation and condensation reactions. Thus, at a temperature of 440 °C, the duration of the process during which light fraction recovery can proceed without a substantial increase in residue viscosity is approximately 10 minutes. As shown in Table 4, during this time, more than 35% by volume of light fractions can be obtained from the initial amount of bitumen, while the residual cracking product retains relatively low viscosity.

The structural and group composition of heavy residues and fractions (n.c. - 280°C) for activated and thermal cracking are presented in Table 5.

Table 5

The results of the study on the structural-group composition of the products of thermal cracking of bitumen with and without the addition of air at a temperature of 440°C.

Hydrocarbons	Composition, % mass.	
	Without air	With air
The structural-group composition of the fraction (n.c.-280°C).		
Olefin hydrocarbons	19.52	13.68
Paraffins, including:	50.66	67.85
- Linear paraffins	24.34	40.37
- Cycloparaffins	8.90	7.05
- Isoparaffins	17.42	20.43
Aromatic hydrocarbons	20.30	16.10
The group composition of the residue.		
Saturated hydrocarbons	9.07	7.5
Aromatic hydrocarbons	43.49	48.41
Resins	16.39	19.08
Asphaltenes	31.05	25.01

Conclusions

1. Activation of the thermal cracking process with atmospheric oxygen significantly increases the rate of light fractions formation (up to 1.6 times) and reduces the process duration by 2–3 times, especially at temperatures of 430–440 °C.

2. Increasing the amount of supplied air has a positive effect on the volumetric yield of light fractions: at 440 °C, more than 35 vol.% was obtained within 10 minutes, which is 15% higher compared to the non-activated process. At the same time, the optimal properties of the heavy residue are maintained.

3. The composition of the obtained fractions indicates a predominance of paraffins in the light products and a decrease in asphaltene content in the residue, which confirms the efficiency of oxygen-activated cracking from both energy and technological standpoints.

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Effect of Acrylic Monomer Formulation on Photocuring and Water Swelling Ability of PVA Hydrogel

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Abstract. *The aim of this research was to develop photocross-linkable hydrogel compositions based on polyvinyl alcohol, photoinitiator, and functional acrylate monomers, to study their cross-linking under UV irradiation, and the swelling ability in water of the obtained photocross-linked materials.*

Keywords: polyvinyl alcohol, benzophenone, functional acrylate monomer, photocross-linking, polymer hydrogel composition.

Introduction

Polyvinyl alcohol (PVA) is one of the most extensively produced synthetic water-soluble polymers globally for nearly a century, still captivating the attention of researchers and technologists. This enduring interest is attributed to its exceptional properties, including a perfect film-forming ability, high hydrophilicity, and the capacity to form hydrogels easily under a variety of conditions and with variable properties. Additionally, PVA belongs to quickly and highly biodegradable polymers [1]; thus, its use has a low impact on the environment. These characteristics have facilitated its wide-ranging applications in diverse fields such as engineering, medicine, pharmaceuticals, cosmetics, biotechnology, and the food industry [2-6].

PVA is mainly a hydrophilic linear copolymer of vinyl alcohol and vinyl acetate, whose properties primarily depend on the degree of polymerization and the degree of hydrolysis. For the formation of stable hydrogels, PVA must be cross-linked. Various physical and chemical cross-linking methods have been developed for this purpose [5-10]. Physically cross-linked hydrogels are not stable and might be destroyed under the influence of various external factors. Among the chemically cross-linked hydrogels, the most stable are hydrogels obtained through the radical mechanism, since the formed cross-linking carbon chains are not susceptible to hydrolysis. Particularly, the work [11] reports on the use of polymer peroxides for cross-linking of PVA. The method allows for achieving high degrees of cross-linking, while its disadvantage is the use of high temperatures for quite a long time to realize this. From this point of view, a promising approach to obtain PVA hydrogels is to apply the photocuring processes initiated by UV irradiation [12].

Important aspects for the production of hydrogel materials are the availability and cost of the starting compounds, as well as the simplicity, energy efficiency, and environmental friendliness of their production processes. Therefore, the development of new PVA-based hydrogel materials using simple technologies is definitely an urgent task today.

The aim of this research was the development of photocross-linkable polymeric hydrogel compositions based on polyvinyl alcohol, photoinitiator, and functional monomers; the study of their cross-linking under UV irradiation, and the swelling ability in water of the obtained photocross-linked materials.

Materials and Methods

Polyvinyl alcohol (PVA) supplied by "JAPAN VAM&POVAL Co" brand JP-18 $\sim[\text{CH}_2\text{CH}(\text{OH})]_a-[\text{CH}_2\text{CH}(\text{O}-\text{COCH}_3)]_b\sim$ with the following characteristics: degree of hydrolysis – 87.0-89.0%, molecular weight – 80 kDa.

Acrylate monomers: acrylic acid (AA), methylene-bis-acrylamide (MBA), 2-hydroxyethyl methacrylate (2-HEMA), and the photoinitiator – benzophenone (BP) were obtained from Merck & Co. AA was vacuum distilled prior to use, other reagents were used as received.

Photocross-linkable compositions were prepared by mixing a 10% aqueous solution of PVA with a solution of BP in AA at their weight ratio in the final solution of 100:1:5, respectively. These compositions exhibited the necessary rheological properties that ensure the formation of uniform films. The compositions were coated onto glass substrates, dried, placed in a PE bag under an inert atmosphere, and then irradiated with a DRT-400 UV lamp at a distance of 10 cm. Experiments were conducted at room temperature; to prevent the samples from being heated by a UV lamp, they were cooled with a fan. After irradiation for a certain time, the samples were removed from the PE bags and subjected to tests for sol-gel fraction content, swelling ability, surface hardness, tensile strength, and maximum elongation.

To determine the sol-gel fraction, the samples were extracted using a Soxhlet extractor for 8 hours, and distilled water was used as the extraction solvent. Subsequently, the samples were dried in an oven at 333 K until a constant weight was achieved. The gel fraction (G) was determined using the following equation:

$$G = \frac{W_f}{W_i} \times 100\% \quad (1)$$

where: G – gel fraction content in the cured polymer film (%); W_i – initial weight of the polymer film before extraction (g); W_f – the weight of dried film after extraction (g).

The swelling of polymer hydrogels in distilled water was studied over a certain period of time. The swelling degree (S) was calculated using the following equation:

$$S = \frac{W_s - W_d}{W_d} \times 100\% \quad (2)$$

where S is the degree of swelling (%); W_s – weight of a hydrogel polymer film soaked with water (g); W_d – weight of a dry polymer film (g).

To determine the swelling rate constant (K) and the equilibrium (maximum) water content in the hydrogel (W_∞), equation 3 [13] was used:

$$\frac{dW}{dt} = K(W_\infty - W)^2 \quad (3)$$

where W is water content in the hydrogel (%); W_∞ – equilibrium (maximum) water content in the hydrogel (%); t – time (min.); K – swelling rate constant (% • min⁻¹).

Results and Discussion

To obtain photocross-linkable composites based on PVA, a photoinitiating system consisting of a BP solution in AA was used. The choice of such a system for PVA curing is explained by the following considerations:

- firstly, BP is well soluble in organic solvents, but almost insoluble in water; to facilitate the introduction of BP into an aqueous PVA solution, it was pre-dissolved in AA, which is well soluble in water; thus, AA serves as a co-solvent for BP, allowing it to be easily introduced into an aqueous PVA solution;
- secondly, as shown by B. Rånby et al. [14], the combination of BP and AA is an effective

system for cross-linking polymers via the photografting mechanism.

Photocross-linkable composite films were irradiated with a UV lamp, as described in the "Materials and Methods" section. The effect of the composition formulation on the gel fraction content after UV curing was investigated (Table 1).

Table 1

Composition #	Photocross-linkable compositions (weight parts)			Gel fraction (%)
	PVA	BP	AA	
1	100	1	5	14.9
2	100	2	10	19.7
3	100	2	5	7.5

Based on the experimental data, it can be concluded that the doubling of the weight parts of the photoinitiating mixture of BP and AA (from 1 wt.% and 5 wt.% to 2 wt.% and 10 wt.% per 100 wt.% of PVA, respectively) did not have a significant effect on the content of the cross-linked polymer, while an increased amount of BP alone had a negative impact on this parameter. Therefore, in subsequent studies, the photoinitiating system of BP and AA was used in amounts of 1 wt. and 5 wt., respectively, relative to the PVA weight.

The influence of UV irradiation time on the gel fraction content of the composites was studied; the results are shown in Figure 1. As can be seen, the content of the cross-linked fraction showed a clear trend to rise with increasing exposure time. However, in the case of using the photoinitiator system consisting only of BP and AC, even after 45 minutes of irradiation, the content of the cross-linked polymer was not high enough, reaching values of about 15%.

To obtain highly cross-linked polymer structures in the composites, the cross-linking agents such as MBA and 2-HEMA were added into the compositions in the amount of 3 wt. per 100 wt. of the matrix polymer. The results of the photocuring of such composites are shown in Figure 1.

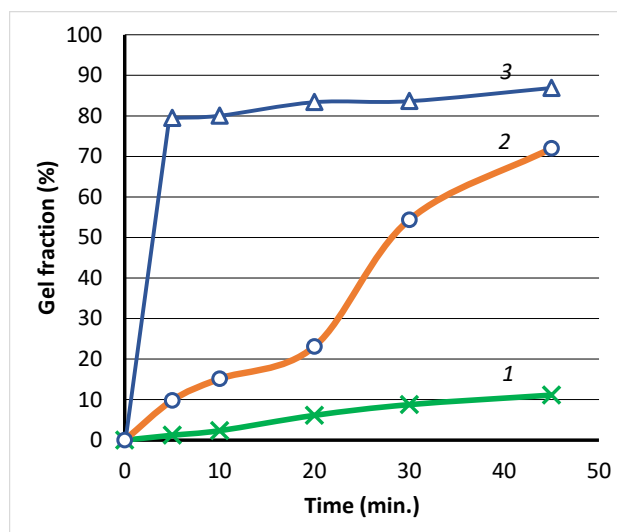


Fig. 1. Dependence of gel fraction content on UV irradiation time of the photocross-linkable composites comprised of: 1 – PVA and BP+AA; 2 – PVA and BP+AA+2-HEMA; 3 – PVA and BP+AA+MBA.

Based on these experimental results, it can be concluded that the photocross-linkable composite comprised of PVA, BP and AC, with the addition of 3 wt. MBA, exhibited the most favourable properties in terms of cross-linking rate and gel fraction content. The data revealed that this composite formed a significant amount of cross-linked polymer even after relatively short

irradiation times. It should also be noted that the introduction of 2-HEMA in the amount of 3 wt. also had a positive effect on the increase in the gel fraction content in the polymer film; however, it grew much more slowly over time of irradiation compared to the composite with the addition of MBA. The latter demonstrated a rapid initial increase in cross-linked polymer content, reaching 79.5% in the first 5 minutes of irradiation; longer exposure time resulted in a slight increase in this parameter, reaching 86.9% after 45 minutes of irradiation.

The degree of swelling in water of the cross-linked PVA-based films was found to be significantly influenced by the cross-linking degree and the type of acrylic monomer employed. The swelling behaviour of the cross-linked PVA films is illustrated in Figure 2.

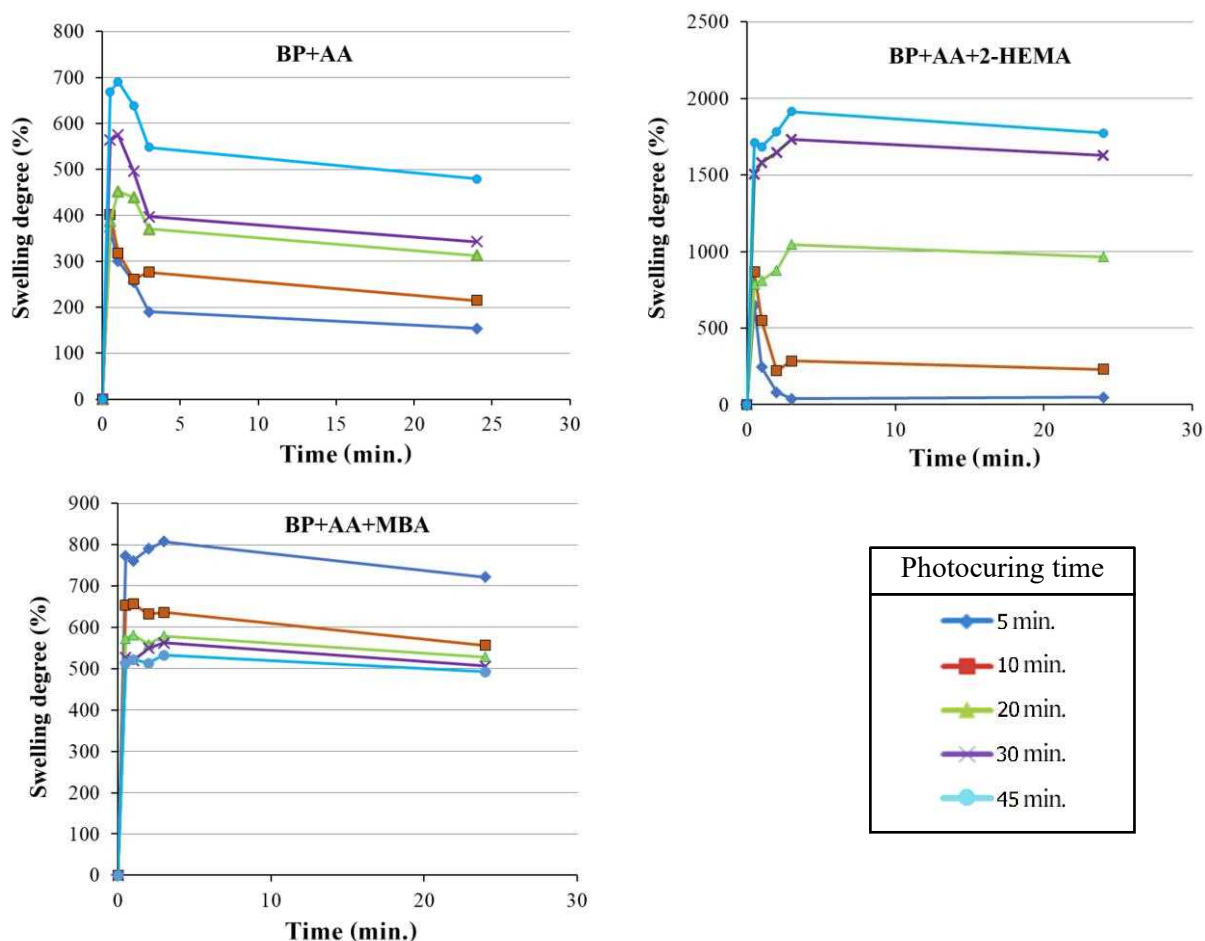


Fig. 2. Swelling kinetics of the PVA films cross-linked with different photocross-linking systems.

The obtained swelling kinetic curves of PVA films evidenced that when immersed in water, all of them readily and quickly absorbed a large amount of water with a sharp increase in their weight by hundreds of times within the first couple of minutes. However, a longer deposition of all the investigated PVA films in water brought about a decrease in the degree of their swelling. The reason for such behaviour was a partial dissolution of a sol fraction of PVA films in water. The lower the content of gel fraction (higher sol fraction) in the cross-linked PVA films, the greater this decrease; i.e., the shorter the time of their UV-irradiation, the greater the weight drop of swollen PVA films during prolonged immersion in water.

Comparing the data presented in Fig. 2, the following conclusions can be drawn.

The highest degree of swelling was achieved when cross-linking was performed using the mixture of BP and AA with the addition of 2 HEMA. The maximum value of almost 2000% of swelling degree was achieved when this composition was exposed to irradiation for 45 minutes,

and a slightly lower value of swelling was achieved for 30 min. of exposure. When this composition was irradiated for 20 min., the swelling degree was almost twice as low; and a shorter exposure time (10 and 5 min.) drastically decreased this parameter. As aforementioned, this decrease was explained by the fact that the uncross-linked polymer (sol fraction) was washed out of the volume of the swollen film and diffused into the aqueous medium. The observed increase in the degree of swelling over the exposure time to UV radiation suggests that at short exposure times, the polymer network was insufficiently cross-linked and contained a significant fraction of the polymer chains lacking cross-links and capable of diffusion into an aqueous medium. To achieve the formation of a tightly cross-linked polymer network, a considerably longer exposure time was required, as Figure 1 evidences.

Table 2

Dependence of swelling kinetics of polymer films on composition and cross-linking time

Composition #	Polymer film composition	Photocuring duration (min.)	Swelling after 24 hours (%)	K ($\%^{-1}/\text{min}^{-1}$)	W_{∞} (%)
1.	PVA+(BP+AA)	5	154	$8.03 \cdot 10^{-4}$	34.5
		10	214	$1.08 \cdot 10^{-3}$	52.9
		20	313	$1.50 \cdot 10^{-3}$	67.6
		30	342	$1.56 \cdot 10^{-3}$	70.4
		45	479	$2.45 \cdot 10^{-3}$	78.7
3.	PVA+(BP+AA+2-HEMA)	5	115	$1.37 \cdot 10^{-3}$	45.5
		10	229	$1.38 \cdot 10^{-3}$	55.9
		20	1015	$1.87 \cdot 10^{-3}$	90.1
		30	1629	$9.54 \cdot 10^{-3}$	93.5
		45	1774	$8.63 \cdot 10^{-3}$	94.3
4.	PVA+(BP+AA+MBA)	5	730	$3.41 \cdot 10^{-2}$	86.4
		10	556	$2.29 \cdot 10^{-2}$	82.0
		20	528	$2.21 \cdot 10^{-2}$	81.3
		30	506	$1.86 \cdot 10^{-2}$	80.0
		45	492	$1.40 \cdot 10^{-2}$	79.4

A similar situation was observed with PVA films, which were cross-linked with the aid of a mixture of BP and AA only (Fig. 2). These films demonstrated a lower swelling degree and significant weight loss in the swollen state upon prolonged contact with water, indicating insufficient cross-linking of the polymer matrix. As a result, such films were unable to maintain their shape and resist dissolution.

Regarding the PVA films cross-linked using BP and AK with the addition of MBA (Figure 2), despite the relatively short UV exposure times, they exhibited high swelling degrees for all the studied samples because of the extremely high cross-linking degree of the polymer matrix. It is interesting that, contrary to previous formulations, this composition showed a strong trend to decrease the swelling degree of the films with increased UV exposure time. This phenomenon can be explained by the fact that, due to its bifunctionality, BMA facilitated the formation of a polymer network with numerous cross-linking centres, which in turn reduced the internodal distance in the polymer network, making it more rigid and less prone to deformation and volume increase, thereby reducing the ability to absorb large amounts of water. It is worth noting that these photocross-linkable hydrogel compositions demonstrated remarkable stability, maintaining their shape even

after 24 hours of immersion in water, although they did exhibit some dimensional changes due to water uptake.

From the graphical dependencies $W = f(t)$, the swelling rate constants (K) and the equilibrium (maximum achievable) water contents in the swollen films ($W_{\infty}\%$) under given conditions were determined. The obtained data are presented in Table 2.

As can be seen from Table 2, the values of the swelling rate constant gradually increased when only BP and AA were used for PVA photo crosslinking, suggesting that the maximum swelling degree was not reached yet in this system.

In the composition with added 2-HEMA, the swelling rate constant also tended to increase with increasing irradiation time up to 30 minutes, reaching a maximum value. Longer irradiation up to 45 minutes brought about a slight decrease in the constant, apparently due to an increase in cross-link density in the polymer matrix, which made it more rigid.

For PVA films cross-linked with the addition of MBA, the maximum degree of swelling, as well as the maximum value of the swelling constant, were reached at the shortest exposure time (5 min.). Longer irradiation time resulted in a decrease in both these parameters, which is explained by an increase in the cross-link density of the polymer matrix, as mentioned previously.

Conclusions

Polymer hydrogel compositions based on PVA, a photoinitiator, and functional acrylate monomers were developed, cross-linking of these compositions under UV irradiation was investigated, and the influence of composition and UV curing conditions on their properties was determined. Strong, highly cross-linked polymer films were obtained by introducing MBA into the composition. Such materials can find application as membranes for nanofiltration, as well as in medicine.

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Preparing the Organic-Inorganic Hybrid Perovskites for the Effective Solar Cell

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Abstract. *The synthesis of organic-inorganic bromide perovskites from aqueous and nonaqueous solutions was carried out, and their crystallographic structure and electronic structure were investigated. The predominant growth of nanoclusters along the [h00] direction was found, which is associated with the use of a polar solvent containing electronegative oxygen atoms. This preferential crystallographic orientation opens up the prospects for efficient transportation of charge carriers in solar perovskite cells.*

Keywords: hybrid bromide perovskite, dimethylformamide, electronic structure, morphology, solar cell materials.

Introduction

Today, the development of efficient solar cells is one of the key areas of green energy development. In addition to existing materials, new high-performance materials with simpler production technologies are constantly being searched for to convert solar energy. Recently, organic-inorganic perovskites $\text{CH}_3\text{NH}_3\text{Pb}(\text{I}, \text{Cl}, \text{Br})_3$ have attracted considerable attention as light-absorbing layers for the design of low-cost and highly efficient solar cells [1-2]. The peculiarities of the perovskite crystal lattice make it possible to create a very efficient light-harvesting layer for solar panels on its basis. When creating these elements, attempts are made to reduce the cost, energy consumption, simplify and speed up the manufacturing process, and achieve maximum stability in various weather conditions [3]. This paper presents methods for the preparation of hybrid organic-inorganic perovskites $\text{CH}_3\text{NH}_3^+\text{PbBr}_3^-$ from aqueous and nonaqueous solutions for efficient light-absorbing layers of solar cells, and investigates their structural characteristics and electronic structure.

Experimental part

Synthesis of $\text{CH}_3\text{NH}_3\text{PbBr}_3$ perovskite from aqueous solution (MAPbBr₃_DMF). The synthesis of hybrid organic-inorganic perovskites $\text{CH}_3\text{NH}_3\text{PbBr}_3$ in the presence of an organic solvent, dimethylformamide (DMF), consisted of two stages. At the first stage, white crystals of methylammonium bromide, $\text{CH}_3\text{NH}_3\text{Br}$, were obtained. Stoichiometric amounts of methylamine CH_3NH_2 (40 wt% aqueous solution) and bromic acid HBr (40 wt% aqueous solution) were added to a 250-mL three-necked round-bottomed flask under continuous stirring at 0 °C for 2 hours to obtain a homogeneous, clear solution of $\text{CH}_3\text{NH}_3\text{Br}$. The methylammonium bromide solution was concentrated at 60 °C on a rotary evaporator for 2 hours. After 24 hours of heating in a vacuum, a

white $\text{CH}_3\text{NH}_3\text{Br}$ precipitate was formed. In the second step, the pre-prepared $\text{CH}_3\text{NH}_3\text{Br}$ and commercial PbBr_2 powder (purity 98+%) were mixed in a 1:1 molar ratio in the organic solvent DMF. After continuous stirring at 60 °C, a clear solution was obtained. To obtain cubic perovskite powder $\text{CH}_3\text{NH}_3\text{PbBr}_3$, the solution was evaporated under reduced pressure at 80 °C to form orange crystals, which were further characterized by X-ray diffraction, infrared spectroscopy.

Synthesis of $\text{CH}_3\text{NH}_3\text{PbBr}_3$ perovskite from aqueous solution (MAPbBr_3). $\text{CH}_3\text{NH}_3\text{PbBr}_3$ polycrystals were prepared by precipitation from bromic acid solutions according to the Poglitsch method [4]. In this procedure, 2.5 g of plumbum (II) acetate trihydrate (99.5 - 102.0%, ACS reagent) was dissolved in 10 mL of a concentrated aqueous solution of HBr (48 wt% aqueous solution) and heated to 90 °C. To this solution was added 2 mL of concentrated bromic acid along with 0.597 g of methylamine, CH_3NH_2 (40 wt% aqueous solution). Orange crystals of about 2 mm in size were formed as the solution was cooled from ~90 °C to room temperature for 72 hours.

The Fourier transform infrared spectra were recorded on a Spectrum BX FT-IR spectrophotometer (Perkin Elmer, USA) using a frustrated total internal reflection (FTIR) detector with a ZnSe crystal. The measurements were performed in the spectral range of 400-4000 cm^{-1} with a resolution of 2 cm^{-1} and an accumulation time of one spectrum in a series of 0.5 s. One experimental series consisted of 128 spectra. All measurements were performed at room temperature. No FTIR corrections of the measured spectra were performed.

X-ray diffraction studies were carried out at room temperature using a Shimadzu LabX XRD-6000 diffractometer using $\text{CuK}\alpha$ radiation ($\lambda = 1.54178 \text{ \AA}$). The diffraction spectrum for phase analysis was acquired using a θ -2 θ scanning scheme with Bragg-Brentano focusing in the range of 2 θ angles from 5 to 70° with a step $\Delta(2\theta) = 0.02^\circ$. The exposure time at each point was 1 second. Measurements were performed at a tube voltage of 35 kV and a current of 30 mA. To identify the phase composition of the sample, we used the Match! 3 program with the built-in COD (Crystallography Open Database - <http://www.crystallography.net/cod/> - 512,072 cards). Indexing of reflexes (assignment of Miller hkl crystallographic indices to each reflex) on diffractograms and calculation of perovskite unit cell parameters were performed using N-TREOR09 of the FullProf Suite Program (version July 2017).

The surface microstructure of the $\text{CH}_3\text{NH}_3\text{PbBr}_3$ perovskite samples was studied using a Tescan Mira 3 scanning electron microscope (SEM).

The X-ray photoelectron spectra (XPS) of the core levels of the studied elements were obtained using an XPS 2400 X-ray spectrometer (Jeol, Japan). The working vacuum during the experiment was 10^{-7} Pa. A magnesium anode with a Mg $\text{K}\alpha$ line energy of 1253.6 eV was used. The energy resolution was 0.1 eV. The calibration of the binding energies was carried out using the 1s carbon line of 284.0 eV.

Results and discussion

To understand the chemistry of the interaction between the initial reagents and to confirm the existence of an intermediate adduct, solvate, the spectral characteristics of the obtained crystals were studied in the infrared range (Fig. 1).

In the studied spectral range, various types of vibrations characteristic of $\text{CH}_3\text{NH}_3\text{PbBr}_3$ perovskite can be observed: stretching vibrations of the C-N bond, strain C-H₃, strain N-H₃, pendular $\text{CH}_3\text{-NH}_3$, asymmetric valence vibrations of the C-H and N-H bonds at 960 cm^{-1} , 1426 cm^{-1} , 1584 cm^{-1} , 1260 cm^{-1} , 2965 cm^{-1} , and 3131 cm^{-1} , respectively [5-6]. However, no peaks corresponding to Pb-Br vibrations were found, since PbBr_2 is transparent in the IR region [7]. For the pure solvent DMF, the vibrational mode of the C=O bond is located at approximately 1671 cm^{-1} , but shifts to the low-wave region to a lower wavenumber of 1653 cm^{-1} for the powder

containing the solvated adduct, the intermediate product $\text{CH}_3\text{NH}_3\text{Br} \cdot \text{PbBr}_2 \cdot \text{DMF}_x$ (x is the number of solvated DMF molecules). It is expected that the $\text{C}=\text{O}$ valence vibrations in the $\text{CH}_3\text{NH}_3\text{Br} \cdot \text{PbBr}_2 \cdot \text{DMF}_x$ powder should be reduced by the interaction of the organic solvent with the Lewis acid of PbBr_2 and $\text{CH}_3\text{NH}_3\text{Br}$ [8].

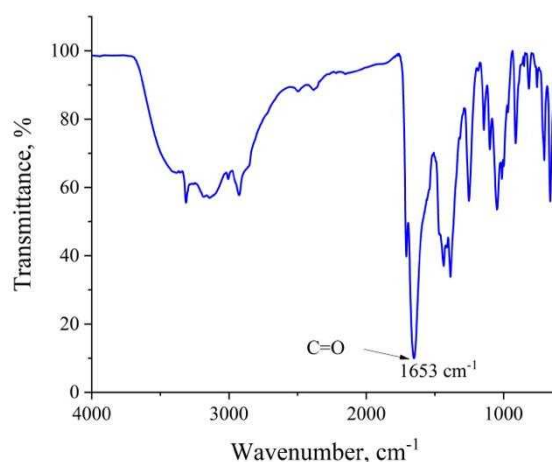


Fig. 1. Infrared spectrum of orange $\text{CH}_3\text{NH}_3\text{PbBr}_3$ crystals obtained from DMF solution.

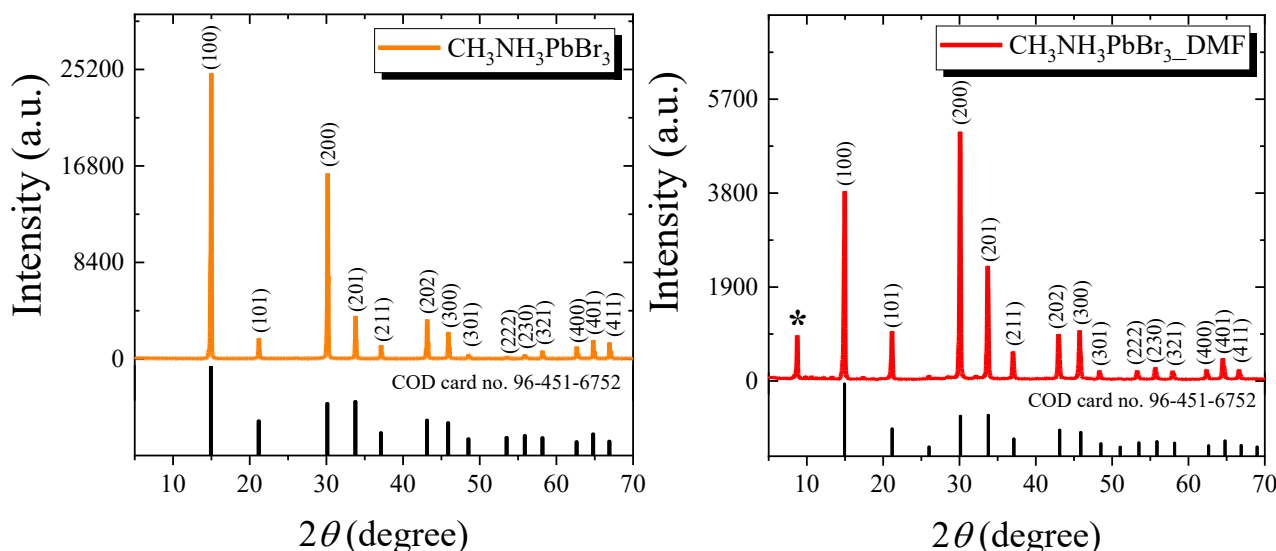


Fig. 2. Comparison of experimental diffractograms of lead organic-inorganic perovskites obtained by precipitation from aqueous solutions (a) and by vacuum crystallization from DMF solution (b) and standard samples from the powder diffraction database (black bars).

The positions and intensities of the reflexes in the experimental diffractograms completely coincide with the corresponding peaks for the diffraction patterns of bromide (COD card No. 96-451-6752) perovskites generated from the crystallographic database. This fact allows us to perform the indexing procedure (assigning a specific Miller index to each diffraction reflection) and confirm the single-phase nature of the obtained samples. Rather narrow diffraction peaks indicate a high degree of crystallinity of organic-inorganic perovskites.

As can be seen from Fig. 2, the appearance of a strong diffraction peak at 8.5° (marked with an asterisk) for the bromide sample $\text{CH}_3\text{NH}_3\text{PbBr}_3 \cdot \text{DMF}$, obtained by crystallization from a DMF solution under reduced pressure, may be due, as some authors argue [9], to the presence of DMF molecules in the compound. According to previous studies, a decrease in the diffraction angle of the intermediate phase indicates that solvent molecules are incorporated/intercalated into the perovskite structure [10]. Based on Bragg's formulation, the diffraction peak from the bromide

phase of $\text{CH}_3\text{NH}_3\text{PbBr}_3$ (Fig. 2) at 14.9° indicates that the distance between layers/planes (100) of the layered perovskite structure is approximately 5.9 Å, while in the intermediate phase $\text{CH}_3\text{NH}_3\text{PbBr}_3 \cdot \text{DMF}_x$, the translation vector along the c-axis increases further (Table 1), and, accordingly, the volume of the crystal lattice in comparison with the desolvated $\text{CH}_3\text{NH}_3\text{PbBr}_3$ sample.

Table 1

Crystallographic parameters of polycrystalline lead perovskites

Sample	MAPbBr ₃ (CH ₃ NH ₃ PbBr ₃)	MAPbBr ₃ DMF (CH ₃ NH ₃ PbBr ₃)
Synthesis method	Precipitation from aqueous solution	Vacuum crystallization from DMFA solution
Phase composition	CH ₃ NH ₃ PbBr ₃	CH ₃ NH ₃ PbBr ₃ + CH ₃ NH ₃ PbBr ₃ · xDMF
Crystall system	cubic	cubic
Spatial group	$Pm\bar{3}m$ (No. 221)	$Pm\bar{3}m$ (No. 221)
Parameters of an unit cell	$a = 5.9290(2)$ Å; $\alpha = \beta = \gamma = 90^\circ$	$a = 5.9568(2)$ Å; $\alpha = \beta = \gamma = 90^\circ$
Volume of the crystall lattice V [Å ³]	208.428(10)	211.374(14)
Number of formula units Z	1	1
Radiographic density D_X [g·cm ⁻³]	3.768	3.715

These XRD results showed that, in general, the growth of nanoclusters was oriented along the [h00] direction. However, the study of the morphology of the samples by SEM showed that at a macroscale of 100 µm, the particles of both $\text{CH}_3\text{NH}_3\text{PbBr}_3$ samples are cubic crystals (Fig. 3, a).

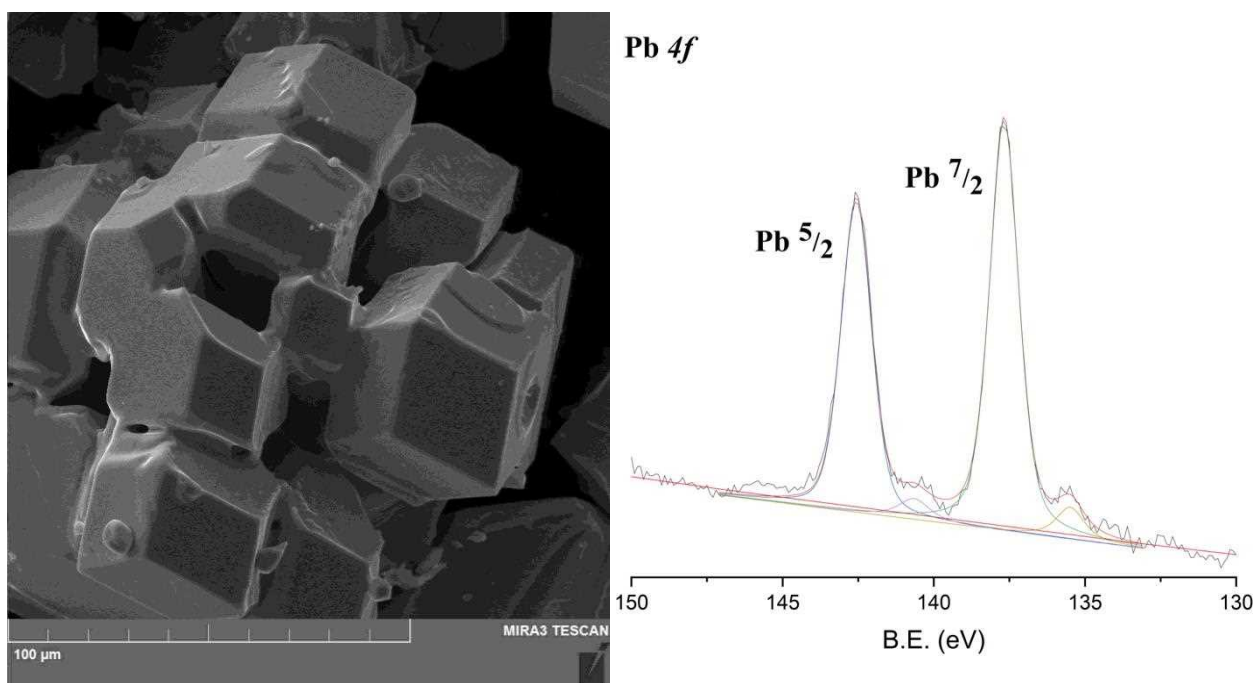


Fig. 3. (a) SEM image of the powder $\text{CH}_3\text{NH}_3\text{PbBr}_3$; (b) – XPS spectra of the core level Pb 4f in $\text{CH}_3\text{NH}_3\text{PbBr}_3$.

The formation of such highly oriented crystals can be attributed to the use of DMF, a polar solvent containing electronegative oxygen atoms. Such a preferential crystallographic orientation

in polycrystalline films is desirable for the efficient transportation of charge carriers in perovskites and metal halide semiconductors.

The study of the electronic structure of the samples by XPS allowed us to establish some chemical instability for the samples obtained from aqueous solutions (Fig. 3b). The XPS spectra of the Pb 4f core level in $\text{CH}_3\text{NH}_3\text{PbBr}_3$ show two intense peaks at 137.9 and 142.5 eV, which reflect the doublets of Pb 4f_{7/2} and 4f_{5/2} and correspond to the Pb-Br bond. In addition, two additional low-intensity peaks are observed, located at approximately 136 and 140.7 eV, which peaks correspond to the metallic state of Pb(0).

Thus, two different chemical states of lead are observed: Pb(+3) and Pb(0). The appearance of the Pb(0) peak in the XPS spectra of perovskite is caused by the interaction of the X-ray beam with the sample [11]. The mechanism of this process is the degradation of MAPbBr_3 to PbBr_2 in a low-pressure XPS chamber, and subsequently of PbBr_2 to Pb(0) during the experiment.

Conclusions

It has been found that the solvent of the dimethylformamide precursor solution affects the early stages of crystallization and induces a preferential orientation in the deposited perovskite samples. Such a preferential crystallographic orientation in polycrystalline films is desirable for the efficient transport of charge carriers in perovskites and metal halide semiconductors, so perovskites synthesized using dimethylformamide are promising for obtaining films.

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Constant Magnetic Field Influence on (Meth)Acrylic Esters Polymerisation in the Presence of Polyvinylpyrrolidone

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Abstract. *The influence of a constant magnetic field on the polymerization of (meth)acrylic esters in composition with polyvinylpyrrolidone has been studied. It has been found that the magnetic field promotes complex formation, accelerates polymerization, and formation of a more ordered structure of copolymers. The obtained materials are characterized by increased hardness, heat resistance, hydrophilicity, and permeability for solutions of low molecular weight substances, making them suitable for application in the production of contact lenses and implants.*

Keywords: polyvinylpyrrolidone, 2-hydroxyethyl methacrylate, magnetic field, polymerization, copolymer, contact lenses.

Introduction

The development of modern science and technology requires the creation of new materials with specified properties. This is particularly relevant in the pharmaceutical and biomedical fields, where there is a growing need for functional polymeric materials. Polyvinylpyrrolidone (PVP) is one of the most promising polymer matrices due to its non-toxicity, water solubility, and ability to form complexes. It is widely used in creating hydrophilic biocompatible copolymers for contact lenses, implants, dialysis membranes, and other medical applications.

Studies of the matrix polymerization of glycol (meth)acrylic esters, particularly 2-hydroxyethyl methacrylate (HEMA), in the presence of PVP have shown that complexation with the monomer accelerates polymerization and can provide initiator-free synthesis. However, this process is sensitive to external factors, in particular oxygen, which reduces the reaction rate and deteriorates the properties of the polymers.

One of the promising ways to influence polymerization is the use of a constant magnetic field (MF), which can change the reactivity of the polymer matrix through orientation, diffusion, and solvation effects. However, despite numerous studies, the mechanism of the influence of MF remains poorly understood, and the results obtained are often contradictory.

Analysis of literature [1-3] indicates the possibility of controlling the polymerization process through the influence of MF on electronic orbitals and the formation of π -complexes. This opens up prospects for controlled modification of the structure and properties of copolymers.

The aim of the work is to investigate the influence of a constant magnetic field on the polymerization kinetics of (meth)acrylic esters in the presence of PVP, as well as to establish patterns in the formation of structure and physicochemical characteristics of the obtained copolymers.

Results and discussion

As (meth)acrylic esters we used HEMA, methyl methacrylate (MMA) and glycidyl methacrylate (GMA). HEMA forms homogeneous compositions with PVP; therefore, for such

systems, block polymerization of compositions was investigated. PVP is not soluble in MMA and GMA; therefore, in this case, polymerization of compositions in a solvent that dissolved all components of the polymer-monomer composition was investigated. Butanol and dimethyl sulfoxide (DMSO) were used as solvents, and benzoyl peroxide (PB) was used as a polymerization initiator.

The block polymerization of HEMA in the presence of PVP was studied in a magnetic field at a ratio of HEMA: PVP=10:0...7:3 wt. parts and in the range of magnetic field strengths $H = 0...31$ kA/m and temperatures 303...323 K.

It was found that MF does not affect the rate of block homopolymerization of HEMA (Fig. 1, cr.5,5'). For compositions containing PVP, MF accelerates polymerization (cr.3,4), and, as in the case of thermally initiated polymerization, the polymerization rate increases proportionally to the increase in the amount of polymer matrix in the composition (cr.1-3,5). If the MF intensity is less than 28 kA/m, a pronounced induction period is observed on the kinetic curves of polymerization.

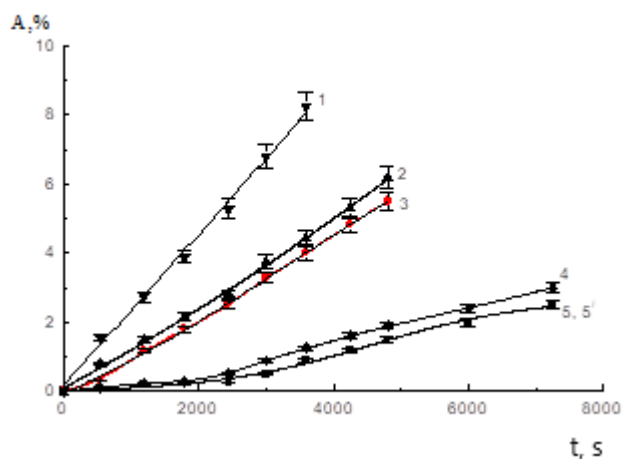


Fig. 1. Dependence of polymer yield (A) on synthesis conditions.

$$[PB]=0.3\%, T = 313\text{ K}, MM_{PVP} = 28 \cdot 10^3.$$

HEMA:PVP, wt. parts: 1 - 7:3; 2 - 8:2; 3.4 - 9:1; 5.5' - 10:0;

MF tension, kA/m: 1 - 3.5 - 31; 4.5' - 0.

The most probable explanation for the observed phenomena can be given based on the mechanism of matrix polymerization of methacrylates in the presence of PVP, which is accompanied by solvation of monomer molecules on the PVP matrix with the formation of a charge transfer complex between the monomer double bond and the tertiary nitrogen of PVP. Complex formation facilitates the dissociation of the double bond in the monomer and causes an increased polymerization rate.

From the research results presented in Fig. 2 and Table 1, it is evident that for both GMA and MMA, the reaction proceeds faster in DMSO than in butanol at the initial stage. At the same time, compositions with GMA polymerize more intensively than those with MMA.

During polymerization in butanol, MMA is the more active monomer. Interestingly, the intensifying effect of the magnetic field for GMA is observed in DMSO medium, while in butanol, the reaction is independent of the magnetic field. However, for MMA, the magnetic field has an effect in butanol medium but shows no influence in DMSO.

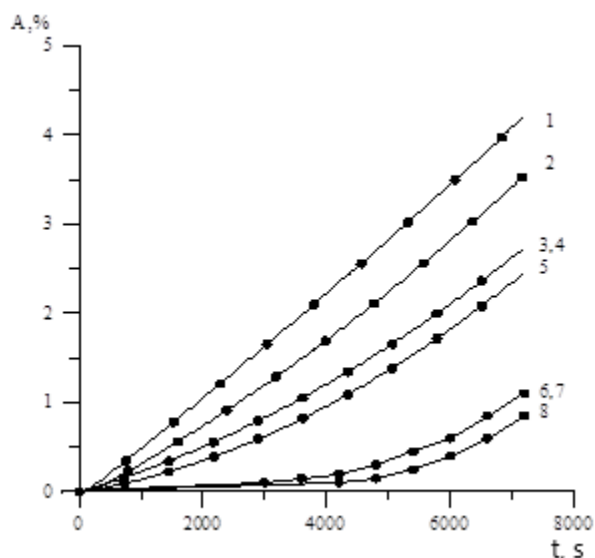


Fig. 2. Effect of the nature of the solvent on the polymer yield (A)
 Composition: $[monomer]:[PVP]:[solvent]:[PB] = 9:1:10:0.02$ wt. parts;
 $N, kA/m: 1.3, 5.7 - 31; 2.4, 6.8 - 0; T = 313 K$.
 Monomer:solvent: 1.2 - GMA: DMSO; 3.4 - MMA: DMSO;
 5.8 - MMA: butanol; 6.7 - GMA: butanol.

Table 1

Kinetic parameters of solution polymerization of hydrophobic monomers

($[monomer]:[PVP]:[solvent]=9:1:10; [PB]=0.2$ wt.%, $T = 313 K$)

Composition	MF tension, N, kA/m	Initial polymerization rate V_{init} , mol/dm ³ ·s
GMA:PVP:DMSO	31	$4.5 \cdot 10^{-5}$
	0	$1.3 \cdot 10^{-5}$
MMA:PVP:DMSO	31	$1.2 \cdot 10^{-5}$
	0	$1.2 \cdot 10^{-5}$
MMA:PVP:butanol	31	$6.0 \cdot 10^{-5}$ tw1
	0	$1.4 \cdot 10^{-6}$
GMA:PVP:butanol	31	$2.4 \cdot 10^{-7}$
	0	$2.4 \cdot 10^{-7}$

The more efficient polymerization of both GMA and MMA in DMSO can primarily be attributed to this solvent's higher polarity compared to butanol, which promotes greater polarization of monomer molecules. Under magnetic field conditions, this also leads to additional orientation and coordination of molecules in the polymer matrix field, followed by aggregation and incorporation into the polymer chain.

To confirm the effect of the magnetic field on the formation of the supramolecular structure of polymers during polymerization, X-ray diffraction studies and a comparative analysis of samples obtained in a magnetic field and by conventional thermopolymerization were conducted. Analyzing the obtained diffractograms (Fig. 3), it can be concluded that copolymers based on PVP synthesized in a constant magnetic field exhibit a more ordered structure with a higher degree of crystallinity compared to polymers synthesized without the application of the field. This trend is observed both in the homopolymerization of HEMA and in its polymerization in combination with PVP.

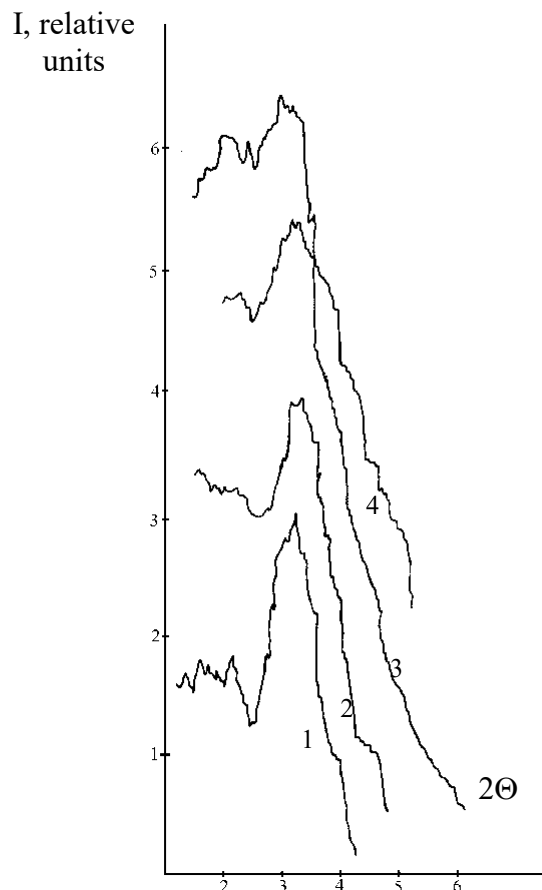


Fig. 3. Diffraction patterns of (co)polymers:
 1,2 – copolymer (polyHEMA: PVP=91:9 wt. parts); 3,4 – polyHEMA
 N , kA/m: 1.3 – 31; 2.4 – 0; $T = 313$ K.

The study of the supramolecular structure of the obtained (co)polymers using X-ray diffraction (Fig. 3) showed that the copolymer sample synthesized in a magnetic field at $H = 31$ kA/m exhibits a more intense maximum in the region of $2\theta = 3.5^\circ$. In this region, the diffractogram of the copolymer synthesized in the magnetic field shows a more pronounced and visibly intense peak characteristic of the crystalline phase compared to the diffractograms of the copolymer obtained without the magnetic field and polyHEMA synthesized in the magnetic field, for which the crystalline peak appears more diffuse and less intense. It was also established that the magnetic field has a greater effect on the ordering of polymer molecules in the case of copolymerization.

The application of a magnetic field to the initial composition during polymer synthesis promotes the formation of a more ordered structure. When comparing the diffractograms of the copolymer and the homopolymer, it should be noted that the homopolymer exhibits a lower degree of ordering compared to the copolymer.

Since polymer materials based on HEMA-PVP compositions are most commonly used in medical practice, particularly for the production of soft contact lenses, it was important to determine their properties, such as water content and swelling coefficient (Table 2). These characteristics are crucial for assessing the durability and comfort of lens use. The higher the hydrophilicity of the polymer, the greater the permeability of the lens to oxygen and tears, which directly contributes to its quality.

When polymers are synthesized in a magnetic field, they have a lower degree of crosslinking, which results in higher water absorption and permeability for dissolved components (Table 2).

Table 2

Water absorption and permeability of (co)polymers

HEMA:PVP, wt. parts	MF tension N, kA/m	Water absorption W, %	Swelling coefficient	Diffusion coefficient, $D_{NaCl} \cdot 10^{13},$ m^2/s	Permeability coefficient, $K_{NaCl} \cdot 10^6, kg/m^2 \cdot s$
10:0	0	34.1	1.03	8.4	91
	31	35.7	1.09	9.3	112
9:1	0	36.5	1.10	8.9	135
	31	38.3	1.14	10.0	149
7:3	0	47.2	1.12	34.9	247
	31	49.1	1.24	41.7	335

The properties of the synthesized copolymers can vary, primarily depending on their composition. Since the polymer material based on HEMA-PVP has found wide application for the manufacture of soft contact lenses [4], which are manufactured by the method of turning with surface polishing, from the studied properties, we chose surface hardness and heat resistance, which determine the suitability of the material for mechanical processing.

The hardness of the polymer samples was determined using a Hepler consistometer. As evident from the obtained results, with an increase in PVP content, the hardness and thermal stability of the polymers increase (Table 3).

Table 3

Influence of synthesis conditions on the hardness and heat resistance of copolymers synthesized in MF ($T = 313\text{ K}$)

HEMA:PVP, wt. parts	MF tension, N, kA/m	(Co)polymer hardness, F, MPa	Vicat heat resistance, T_v , K
10:0	0	200±5	357±1
	31	278±5	378±2
8:2	0	288±5	369±1
	31	333±8	383±2
7:3	0	296±7	372±1
	31	340±8	385±2

Obviously, with an increase in PVP content in the composition, the number of crosslinks in the polymer increases, both chemical and physical (the latter can disappear when swelling in water), and consequently, the network density increases and the kinetic mobility between network nodes decreases, resulting in increased hardness and heat resistance of the polymer samples. Although for polymers synthesized in MF, the density of the network formed by chemical crosslinking units is lower, which should lead to a decrease in the hardness and heat resistance of polymers, we observe an increase in these parameters. This phenomenon confirms that in MF, apparently, a polymer with a more ordered structure is formed, which causes its lower defect content. This idea is confirmed by the results of X-ray phase and differential thermal analysis [5], which determined that polymers obtained in MF have a more ordered structure, close to crystalline.

The influence of the conditions for obtaining polymers, in particular the tension of the MF, on their physical and mechanical properties is most clearly manifested for the homopolymer (Table 2). The higher values of hardness and heat resistance for the samples obtained in the MF can be explained by the greater mobility of monomer molecules in the monomer medium, and,

accordingly, their stronger dipole-dipole interaction in the MF which causes the formation of a more ordered structure, compared to PVP copolymers, and is reflected in the properties of homopolymers.

Conclusion

The obtained results confirm that a constant magnetic field affects the polymerization of (meth)acrylic esters in the presence of polyvinylpyrrolidone, accelerating the process due to complex formation between the monomer and polymer matrix. It has been proven that the magnetic field promotes the formation of a more ordered supramolecular structure of copolymers, which is confirmed via the X-ray phase analysis results. Copolymers synthesized under magnetic field conditions are characterized by higher indicators of surface hardness, heat resistance, and permeability for low-molecular substances compared to polymers obtained without the magnetic field application. It was found that the MF effect on the polymerization process considerably depends on its intensity: at values higher than 28kA/m, a decrease in the induction time of the reaction and an increase in the rate of polymerization have been observed. The increased hydrophilicity of the synthesized copolymers makes them promising for application in soft contact lenses and the production of medical implants. The obtained results testify to the possibility of using a magnetic field as a tool for regulating polymerization kinetics as well as forming the structure of copolymers, opening up new prospects for creating biocompatible materials with specified properties.

Acknowledgments

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Fundamentals of the Technology of Obtaining Interactive Materials for Use in Catalysis and Biosensors in the Context of Food Freshness Assessment

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Abstract. *This paper explores the use of interactive materials for application in catalysis and biosensing for food freshness assessment. Through a detailed examination of material properties, synthesis methods, and functionalization techniques, we elucidate how these innovative materials can optimize food safety and quality control.*

Keywords: biosensor, catalysis, microgel, food spoilage, smart packaging.

Introduction

Food safety and quality have become paramount concerns given the rising global population and consequent demand for safe, fresh food products. Traditional methods for assessing food freshness often fall short in terms of accuracy and efficiency. With the advent of modern technology, novel approaches employing catalysis and biosensors have emerged as viable solutions. Food freshness assessment is traditionally conducted through sensory evaluation, chemical tests, or microbiological analysis. However, these methods are often time-consuming and can lack specificity.

Types of food spoilage

Meat spoilage can be caused by natural processes such as lipid oxidation or autolytic enzymatic processes occurring in the muscles after slaughter. Several factors are responsible for microbial contamination of meat, such as bacterial flora of the animal, treatment during slaughter, evisceration and processing, temperature control during slaughter, the type of packaging used, etc.

Spoilage of fish is a complex process caused by the action of enzymes, bacteria, and chemical components.

An increase in pH may indicate the process of autolysis (breakdown of proteins under the action of enzymes). The hypoxanthine content in fish indicates the degree of its freshness. Hypoxanthine is formed by the breakdown of ATP, which is the main component of fish muscle nucleotides. The accumulation of hypoxanthine gives fish muscles a bitter aftertaste, which is accompanied by the loss of the taste of fresh fish.

Breakdown of amino acids leads to the formation of primary amines. Examples are the formation of histamine from histidine, arginine from glutamic acid, etc. This bacterial action can cause food poisoning in extreme cases. A high concentration of urea in the meat of some fish

decomposes microorganisms into ammonia. The formation of ammonia is accompanied by an unpleasant smell.

Spoilage of milk and dairy products leads to an unpleasant taste and smell, as well as a change in texture and appearance. The main carbohydrate in milk is lactose. Microorganisms that produce a lactose-hydrolyzing enzyme (lactase or β -galactosidase) have an advantage over those that cannot metabolize lactose. Milk fat can be hydrolyzed by microbial lipases to form low molecular weight volatile fatty acids (butyric, caproic, and capric). The presence of substances such as ethanol, ethyl ethers, amino acids, lactates, and acetates in dairy products may indicate the development of bacterial contamination of the product, which, in turn, can negatively affect human health.

Evaluation of smart sensors

Smart sensors are devices that can detect and respond to environmental changes. In the context of food freshness, these sensors can monitor various parameters, such as temperature, humidity, and gas emissions, which are critical indicators of food quality.

Smart packaging can include sensors that provide information about food quality through the entire food chain, composition, storage conditions, and bacterial accumulation [1]. The most widespread commercial sensors today are time temperature sensors (TTI) that provide tracking compliance with the temperature chain during transportation and storage, which allows the consumer or the manufacturer to assess the status of the product [2]. For example, the Monitormark™ TTI sensor developed by 3M™ (USA) is designed to monitor the thermal impact on fish and dairy products during storage and transportation below 20 °C [3]. Another example is the Coolvu indicator developed by FreshPoint (Switzerland), which includes a transparent label that provides a visual change to inform consumers of a change in product quality. However, such decisions only show the fact of violation of the temperature regime or shelf life, and are not sufficient grounds to judge whether the product has spoiled or not.

A more effective solution is the use of sensors with indicators that are sensitive to changes in pH or the accumulation of specific substances (markers) that are formed during food spoilage [4].

Important characteristics of a biosensor are its specificity, sensitivity, reliability, portability, and simplicity. To date, there are no commercial biosensors for smart packaging, although several prototypes are being developed. For example, SIRA Technologies (Pasadena, California, USA) is developing a biosensor/barcode called the Food Sentinel System for detecting pathogens in food packaging (Ayala and Park 2000; Anonymous 2004f). In this system, specific antibodies to pathogens are attached to the membrane-forming part of the barcode; the presence of contaminating bacteria causes a localized dark band to form, making the barcode unreadable when scanned. Toxin Alert (Ontario, California, USA) is also developing a diagnostic system called Toxin Guard that incorporates antibodies into plastic packaging films to detect pathogens (Anonymous 2000; Bodenhamer 2002). When the antibodies come into contact with the target pathogen, the packaging material displays a clear visual signal to alert the consumer, retailer, or inspector.

This system is designed to detect gross contamination, as it is not sensitive enough to detect very low levels of pathogens that can cause disease.

The main requirements for the transition to commercially available biosensors are miniaturization, automated analysis, low reagent consumption, portability, minimal time or user skills, and communication [5].

Enzymatic biosensors are based on the close contact of enzymes with transducers. The principle of this type of biosensor is based on the quantification of the inhibitor, measuring the enzymatic activity in the absence and presence of the inhibitor. Inhibition studies are often a key point in the clinical field, as some drugs are based on the inhibition of key enzymes in biological pathways, while other inhibitors are considered toxic compounds; thus, enzyme inhibition-based biosensors are reliable tools for the detection of many toxic compounds.

Primary product composition determination

The object of study is chicken fillet.

Table 1

Determination of primary characteristics is carried out to identify potential markers of spoilage.

Quality indicator	Method	Sample 1	Sample 2
Protein value, %	DSTU ISO 937	21.92	19.36
Fat value, %	DSTU ISO 1442	63.75	69.59
Moisture value, %	DSTU ISO 1443	14.09	11.45
Ash content, %	DSTU ISO 936	1.28	1.12

The presence of off-flavors in meat during storage can be caused by the decomposition of amino acids. For this reason, the amino acid profile of chicken fillets was analyzed using a Sykam amino acid analyzer with preliminary derivatization.

Table 2

Amino acid	Value, %	Functional group
Valine	0.386	Amine
Proline	1.343	Amine
Phenylalanine	0.118	Amine
Leucine	0.327	Amine
Isoleucine	1.545	Amine
Histidine	0.748	Amine
Glycine	0.746	Amine
Glutamic acid	2.141	Amine
Arginine	0.992	Amine
Aspartic acid	1.416	Amine, aldehyde
Alanine	1.425	Amine
Threonine	0.592	Hydroxyl, amine
Methionine	0.841	Amine, sulfide
Lysine	0.992	Amine
Tyrosine	0.856	Amine, hydroxyl
Serine	0.526	Amine
Cysteine	1.259	sulfide

Taking into account the concept of rational chemosensor design and literature search, copper(II) sulfate was isolated for the detection of hydrogen sulfide vapor.

Paper sensors were prepared from ash-free “Blue Ribbon” paper, which was soaked in a 15% aqueous solution of copper(II) sulfate pentahydrate or a 5% ethanol solution of phenolphthalein and dried. The sensor was placed 1 cm above the meat. As a control, sensors based on copper sulfate and phenolphthalein were used, which were sealed in a Petri dish.

Chilled chicken fillet was distributed in 250 g portions in three sealed containers of 1 liter. The first container was made of food-grade plastic and was kept in a refrigerator at 2-4 °C. The second container, a glass hermetically sealed exciter, was kept in a dark place at 16-18 °C. The

third container, a vacuum desiccator, was kept in a dark place at a temperature of 16-18 °C, but additionally, the container was vacuumed with a water jet vacuum pump to 20 mm Hg. The data were taken every 12 or 24 hours and recorded visually according to the color scale: “no change”, ‘slight change’, ‘saturated’, as well as by the ‘presence’ or ‘absence’ of an unpleasant odor. The number of replicates was three.

Table 3

Results of the initial diagnosis of the sensitivity of the proposed sensors to meat spoilage markers.

Exposition time	Container №1	Container №2	Container №3	Control
0 h	no change	no change	no change	no change
12 h	no change	no change	saturated	no change
24 h	no change	slight change	-	no change
36 h	no change	saturated	-	no change
48 h	no change	-	-	no change
72 h	no change	-	-	no change
96 h	slight change	-	-	no change

Conclusions

In all experiments, the phenolphthalein-based sensor was not effective, which can be explained by the fact that phenolphthalein changes color only in aqueous solutions.

Sensors based on CuSO₄ proved to be effective for the diagnosis of hydrogen sulfide. It should be noted that there is a clear bright color change that does not disappear. In addition, in container No. 1, after 96 hours, the sensor “slightly” changed color, but there was no unpleasant odor from meat spoilage markers, which may indicate the effectiveness of this sensor at very low concentrations.

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Influence of Dispersion Medium Parameters on Suspension Polymerization of Methacrylic Esters in Presence of Polyvinylpyrrolidone

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Abstract. *The influence of the solubility parameter on the regularities of obtaining hydrogel suspensions based on copolymers of 2-hydroxyethyl methacrylate and glycidyl methacrylate with polyvinylpyrrolidone has been investigated. The effect of the solvent nature on diffusion processes in suspension polymerization, the dispersive characteristics of hydrogel particles, and the polymerization kinetics have been established.*

Keywords: polyvinylpyrrolidone, 2-hydroxyethylmethacrylate, solubility parameter, suspension copolymerization, hydrogel.

Introduction

Polymeric suspensions with a narrow particle size distribution, predetermined chemical composition, and well-defined structure serve as a fundamental basis for developing drug delivery systems and biologically active substance carriers. From both a scientific and applied perspective, polymeric spherical particles obtained via suspension homopolymerization of methacrylic monomers, such as 2-hydroxyethyl methacrylate (HEMA) and glycidyl methacrylate (GMA), or their graft copolymerization with polyvinylpyrrolidone (PVP) in the presence of crosslinking agents in inert solvent media [1,2] are particularly promising. It is known that such (co)polymers are biocompatible and are effectively used in medicine for the production of contact lenses, artificial intraocular lenses, (hemo)dialysis membranes, dental filling and impression materials, osteoplastic silver-containing composites for bone tissue replacement, and other applications [3-8].

A key challenge in the suspension polymerization of such compositions is the selection of a solvent that can dissolve water-soluble components (HEMA and PVP) while remaining immiscible with water or having limited solubility in it, thereby preventing the diffusion of monomer-polymer composition components into the aqueous phase. Consequently, research on the selection of an appropriate inert solvent to be added to the monomer phase, characterized by a partition coefficient significantly greater for the monomer than for water, is crucial. A critical parameter for evaluating the suitability of a solvent for the polymerization of a specific monomer is the solubility parameter, which reflects the polarity of the reaction medium and controls the critical molecular weight [2].

Results and discussion

During the suspension (co)polymerization of the investigated water-soluble polymer-monomer systems, the use of water as a dispersion medium is complicated by the possible dissolution of both the monomer (HEMA) and PVP. Therefore, to develop a suspension polymerization technology, studies were conducted to select the most effective solvents among higher alcohols, particularly cyclohexanol (CH), nonanol, decanol (DC), and their mixtures, suitable for ensuring the formation of spherical particles with sizes ranging from 0.1 to 2 mm.

Diffusion studies of water-soluble components from the organic (polymer-monomer) phase revealed a slight transfer of HEMA into the aqueous phase during the initial stages of polymer particle formation (Fig. 1), with diffusion virtually ceasing after 1–1.5 hours.

The dissolution of PVP in the monomer reduces the diffusion rate of HEMA into the aqueous phase. The highest monomer diffusion was observed when DC was used as the organic phase, whereas the lowest diffusion occurred with a CH-DC mixture. PVP also diffused from the dispersion phase into the dispersion medium during the initial stage, but in significantly smaller amounts (1.6% per hour).

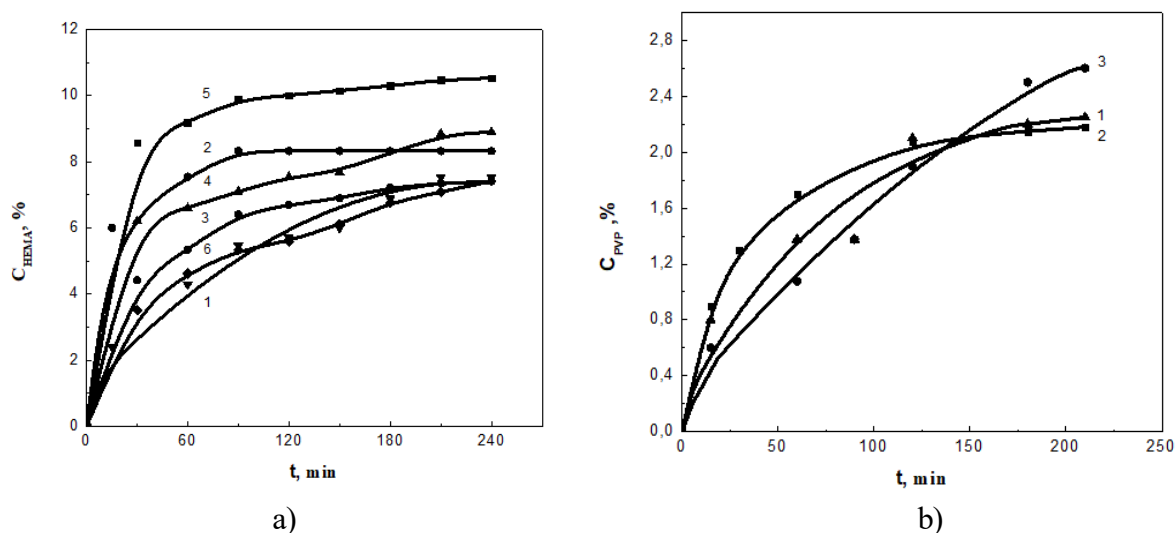


Fig. 1. Kinetics of diffusion of HEMA (a) and PVP (b) from the organic phase into the aqueous phase. $T=293 \text{ K}$.

a) $[\text{HEMA}]=1.9 \text{ mol/l}$. Organic phase: 1– CH;
2 – DC; 3 – CH:DC = 1:1; 4...6 – 8% PVP solution in:
4 - CH; 5 – DC; 6 – CH:DC = 1:1.

b) Organic phase, wt. parts:
1– HEMA:PVP:CH = 8:2:15;
2 – HEMA:PVP:CH:DC = 8:2:7.5:7.5;
3 – HEMA:PVP:DC = 8:2:15.

An important factor determining the efficiency of suspension polymerization is the monomer distribution coefficient between the organic and aqueous phases. It is known that for successful dispersion polymerization, the monomer's distribution coefficient should be as high as possible in the organic phase and as low as possible in the aqueous phase [9]. The determined distribution coefficients for the studied HEMA–PVP compositions were $K_{\text{distrib.1}}=13.1$; $K_{\text{distrib.2}}=11.2$; $K_{\text{distrib.3}}=13.1$; $K_{\text{distrib.4}}=10.5$; $K_{\text{distrib.5}}=8.6$; $K_{\text{distrib.6}}=12.9$. In view of these results, the compositions corresponding to organic phases 1, 3, and 6 (Fig. 1a) are the most suitable.

To confirm the appropriateness of the selected solvents for the polymerization of the HEMA/PVP composition, interfacial tension measurements at the organic phase–water interface were performed (Table 1), which demonstrated an increase in interfacial tension when DC was present in the organic phase.

Table 1

Solubility parameters and interfacial tension of solvent and monomer mixtures

Composition of mixtures, vol. parts				Solubility parameter, δ (MJ/m ³) ^{1/2}	Interfacial tension, $\sigma_{1/2}$, N/m
HEMA	CH	DC	H ₂ O		
—	15	—	50	43.48	10.24
—	—	15	50	43.15	14.39
—	7.5	7.5	50	43.31	15.59
8	11.25	11.25	42.5	39.29	—
8	7.5	7.5	50	41.59	—
8	2.5	2.5	60	44.48	—

Based on diffusion studies, interfacial tension, and calculated solubility parameters, the CH-DC mixture was selected as the inert solvent for the dispersed phase in the suspension polymerization of HEMA-PVP compositions.

For compositions containing another methacrylic ester (GMA), where the monomer is hydrophobic and PVP remains hydrophilic, solvent selection for the dispersion phase in the GMA-PVP system was investigated using various solvents: DC, CH, their mixtures, dioxane, benzene, and toluene (TL). Polymerization synthesis using TL as the solvent resulted in agglomerates, whereas employing DC produced non-spherical polymer particles. Both dioxane and CH proved unsuitable for conducting the granule copolymerization of GMA with PVP, as equilibrium was disturbed over time, leading to droplet coalescence and the formation of a homogeneous swollen polymer block. Analysis of the PVP content in the dispersion medium revealed significant diffusion of PVP (80 wt.% per hour) from the polymer-monomer phase containing these solvents into the aqueous phase. The addition of a TL/DC mixture to the GMA-PVP composition reduced the rate of PVP diffusion from the organic phase to the aqueous phase. The minimal diffusion was observed with a TL/DC volumetric ratio of 1:3. Conversely, an increase in the TL content in the organic phase resulted in an increased diffusion rate and higher limiting value of PVP diffusion (Fig. 2).

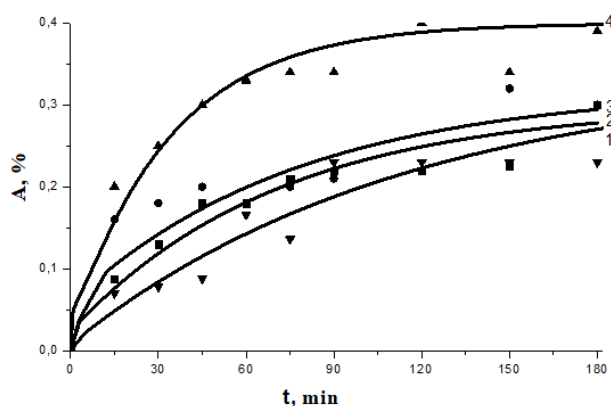


Fig. 2. Kinetics of diffusion of PVP from the organic phase containing GMA into the aqueous phase.

$T=293$ K, $[GMA]=2.9$ mol/l, $[PVP]=5.6$ wt.%.

Organic phase TL:DC, vol. parts:
1 – 1:3; 2 – 0:1; 3 – 1:1; 4 – 3:1.

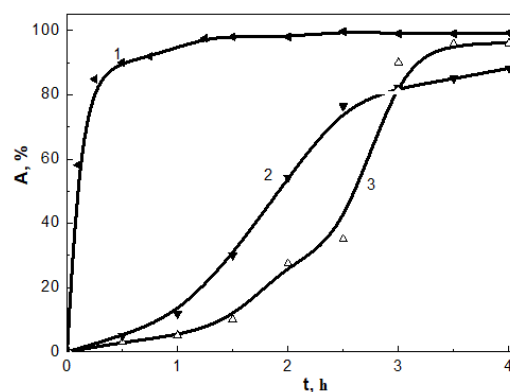


Fig.3. The influence of the solubility parameter δ on the kinetics of suspension polymerization of compositions.

[org. phase]:[H₂O] = 1:2.5 wt. parts
 δ , (MJ/m³)^{1/2}:

1 – 42.300 (GMA:PVP = 8:2 wt. parts);
2 – 42.670 (HEMA:PVP = 8:2 wt. parts);
3 – 42.275 (HEMA:PVP = 10:0 wt. parts).

The nature of the monomer significantly influences both the solubility parameter of the compositions and the polymerization rate. It was established that the polymerization rate of compositions

containing GMA is substantially higher than that for those with HEMA (Fig. 3). Considering the similar reactivity of HEMA and GMA in the homogeneous copolymerization with PVP [6], we attribute the marked differences observed in the dispersion systems to interphase interactions and the interaction parameters between the monomer and the solvent. Compositions containing GMA exhibit lower solubility parameter values ($\delta_{\text{GMA}}=19.36 \text{ (MJ/m}^3)^{1/2}$) compared to HEMA compositions ($\delta_{\text{HEMA}}=23.30 \text{ (MJ/m}^3)^{1/2}$), which is one of the primary reasons for their enhanced reactivity in suspension polymerization (Fig. 3).

The calculated distribution coefficients for the GMA–PVP compositions are presented in Table 2. Based on these findings, the use of a TL/DC mixture as the organic solvent for the dispersion phase in the suspension polymerization of GMA–PVP compositions is justified.

A critical aspect in suspension polymerization is the controlled regulation of the granule size distribution of the polymers. The solubility parameter is one of the factors that undoubtedly affects both the size and shape of the polymer suspensions. Therefore, investigating the particle sizes and the polydispersity index as functions of the solubility parameter is of significant technological importance.

The most uniform particles, having the smallest diameter (and consequently the highest specific surface area), were formed at $\delta = 42.300 \text{ (MJ/m}^3)^{1/2}$, corresponding to an organic phase solvent ratio of DC:TL = 1:1 vol. parts.

Table

Distribution coefficients of composition components in organic and aqueous phases

Composition of mixtures, vol. parts				Distribution coefficient	
GMA	PVP	TL	DC	in organic phase	in aqueous phase
4	1	—	5.6	32.80/31.85	0.03/0.031
4	1	1.4	4.2	43.78/35.83	0.022/0.028
4	1	4.2	1.4	82.57/24.57	0.012/0.041
4	1	5.6	5.6	170.9/34.40	0.006/0.029
4	-	—	5.6	24.08	0.040
4	-	5.6	5.6	31.86	0.031

* numerator – for GMA; denominator – for PVP

Our studies revealed that the influence of the solubility parameter on the average particle size in the suspension polymerization of GMA–PVP compositions exhibits a pronounced extremum, with a minimum particle diameter observed at $\delta = 42.300 \text{ (MJ/m}^3)^{1/2}$ (Table 3).

Table 3.

Influence of the solubility parameter δ on the dispersion characteristics of granular copolymers of PVP–polyGMA.

(GMA:PVP = 8:2 wt.parts; $T = 348 \text{ K}$; $\omega_{\text{rotation}} = 270 \text{ rpm}$; $C_{\text{stab}} = 1 \text{ wt.}\%$; $[PB] = 1 \text{ wt.}\%$)

Composition of mixtures, vol. parts				Solubility parameter, $\delta \text{ (MJ/m}^3)^{1/2}$	d_n , mm	d_w , mm	PDI	Maximum fraction content, %
GMA	DC	TL	H ₂ O					
8	11.2	0	53	42.381	0.925	1.241	1.342	19
8	8.4	2.8	53	42.341	0.760	1.164	1.531	21
8	7.4	3.8	53	42.326	0.626	0.910	1.451	26
8	5.6	5.6	53	42.300	0.467	0.584	1.251	35
8	3.8	7.4	53	42.274	1.336	1.728	1.294	12
8	0	11.2	53	42.220	agglomerates			—

If the solubility parameter falls below this value as a result of an increased TL content in the organic phase, a sharp increase in particle diameter occurs, eventually leading to agglomeration. When TL alone was used as the organic phase solvent (without DC), the formation of granular particles was unsuccessful.

Studies on the influence of the solubility parameter of compositions containing hydrophilic HEMA and PVP on the average particle diameter and polydispersity index demonstrated a similar effect. This dependency was observed both for varying solvent concentrations at a constant ratio and for a constant solvent content at different ratios. With an increase in the solubility parameter, i.e., with an increase in the concentration of CH in the organic phase, the size of the polymer particles decreases. The effect of the solubility parameter on the particle polydispersity also shows an extreme behavior. The most uniform particles were obtained with a CH content of 20–30 wt.% in the composition. For HEMA compositions, a decrease in the concentration of the inert solvents CH and DC in the organic phase leads to an increase in the solubility parameter, resulting in suspensions with smaller particle sizes and a narrow size distribution. The most uniform particles were achieved at an inert solvent (CH + DC) content of 10 wt.% in the organic phase.

Conclusion

In summary, the performed investigations demonstrate that the solubility parameter is a crucial and effective factor influencing both the kinetics of suspension copolymerization of methacrylic esters, such as HEMA and GMA, with PVP and the particle diameter and granule size distribution, which in turn determine the potential applications of the resultant polymers.

The diffusion of water-soluble components from the organic (polymer-monomer) phase was studied, and a slight transition of HEMA and PVP into the aqueous phase was observed at the initial stages of polymer particle formation. However, after 1–1.5 hours, diffusion practically ceased. The dissolution of PVP in the monomer reduced the diffusion rate of HEMA into the aqueous phase. The lowest monomer diffusion was observed when a mixture of CH and DC was used as the organic phase.

The interfacial tension was investigated, and the solubility parameter of HEMA–PVP compositions was calculated. Based on the results, a mixture of DC and CH was selected as an inert solvent for the dispersed phase. The use of an organic solvent mixture of TL and DC for the dispersed phase in the suspension polymerization of GMA–PVP compositions was substantiated.

It was established that the polymerization rate of compositions containing GMA was significantly higher than that of HEMA. The influence of the solubility parameter on the average particle size in the suspension polymerization of GMA–PVP compositions exhibited a distinctly extreme nature. The most uniform and smallest-diameter particles were formed at a solvent ratio in the organic phase of DC:TL = 1:1 vol. parts. For HEMA-based compositions, a decrease in the concentration of inert solvents CH and DC in the organic phase led to an increase in the solubility parameter, resulting in the formation of smaller suspensions with a narrow size distribution.

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OPTIMIZATION OF BIOCHEMICAL PROCESSES AND BIOENGINEERING

Exploring the Potential of Organophosphorus Compounds as Chelators for Enhancing Zinc Bioavailability in Agriculture

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Abstract. *This study explores the complexation of zinc ions by organophosphorus compounds as potential agricultural chelators. Compared to APCA chelators, the results show similar complexation properties, with organophosphorus chelators potentially offering superior biodegradability, highlighting their promise for more sustainable agricultural practices.*

Keywords: chelates, agriculture, organophosphorus compounds, micronutrients, zinc, differential pulse voltammetry.

Introduction

According to the UN report „World Population Prospects 2024”, the global population is projected to increase significantly in the upcoming decades. At the same time, climate change is impacting agriculture by reducing yields, altering growing seasons, and increasing extreme weather events. In the face of these changes, one of the key global challenges is ensuring an adequate food supply for the growing population while simultaneously reducing the negative impact of agriculture on the environment. Intensifying agricultural production, although necessary, carries the risk of soil degradation, water pollution, and reduced biodiversity [1, 2].

Plants require many nutrients for growth and proper functioning, which they mainly absorb from the soil in the form of assimilable chemical compounds. Liebig’s Law of the Minimum states that plant growth is limited by the nutrient in the least supply relative to demand, regardless of the abundance of other nutrients. Therefore, a key goal of agriculture is to provide plants with all the essential nutrients through proper fertilization, ensuring their healthy growth and functioning. Both mineral and organic fertilizers are commonly used for this purpose; however, their excessive application can lead to environmental pollution. To reduce the use of agrochemical products, a comprehensive fertilization approach is necessary - one that not only supplies essential nutrients but also enhances their bioavailability under challenging soil conditions [3, 4].

Compounds with chelating properties enable effective delivery of micronutrient ions to limestone and alkaline soils. Chelators contain at least two donor groups in their structure, which can form stable, claw-like structures - known as chelates - by binding metal ions through coordination bonds. This prevents metal ions from precipitating or becoming immobilized in the soil, ensuring they remain soluble and accessible to plants. As a result, chelators improve the efficiency of micronutrient uptake, supporting plant growth and development, even in challenging soil conditions where essential elements might otherwise become unavailable [5].

Currently, aminopolycarboxylate (APCA) chelators, such as EDTA, DTPA, and EDDHA, are widely used in agriculture due to their stability and ability to efficiently complex micronutrients

over a wide pH range. However, APCA chelators have a low biodegradation rate, leading to bioaccumulation in the environment. They can also continue to complex heavy metal ions like lead, cadmium, and mercury, remobilizing them into the environment and posing ecological risks [6].

In response to these challenges, increasing attention is being given to the development of innovative chelators. A promising alternative to APCA chelators are organophosphorus compounds, which combine high efficiency in micronutrient stabilization in a wide pH range with improved biodegradability [7].

The role of zinc in plant nutrition

Zinc (Zn), present in plants in its ionic form (Zn^{2+}), is an essential micronutrient for plant growth and development, playing a crucial role as a catalytic, structural, and regulatory cofactor in numerous enzymatic processes. It is vital for chlorophyll synthesis, protein and carbohydrate metabolism, and the biosynthesis of growth hormones like indoleacetic acid. Despite its importance, Zn deficiency is one of the most widespread micronutrient deficiencies, particularly in calcareous, sandy, and peat soils, as well as soils high in phosphorus and silicon [8-11].

Zn deficiency in plants leads to stunted growth, leaf chlorosis, shortened internodes and petioles, and the characteristic rosette symptom in dicotyledons. It can also reduce crop quality, increase susceptibility to high light or temperature stress, and make plants more vulnerable to fungal infections. The availability of Zn is influenced by soil type, pH, and interactions with other nutrients that may inhibit its uptake. Additionally, Zn applied as fertilizer often forms insoluble complexes, limiting its bioavailability to plants. Addressing Zn deficiency is crucial for maintaining plant health, productivity, and resistance to environmental stressors [8-11].

Aim of work

Regulation (EU) 2019/1009 of the European Parliament and of the Council of 5 June 2019 establishes requirements for fertilizing products, including the necessity for at least 80% of the declared micronutrient content in micronutrient fertilizers to be in a chelated form to ensure their effectiveness and bioavailability for plants [12].

Given these regulatory standards, the study aimed to evaluate the complexation degree of zinc with various organophosphorus compounds in an aquatic environment, in the presence of the supporting electrolyte. The research focused on assessing the impact of different pH and different chelators on the molar ratios of zinc ions to zinc complexes, providing insights into their potential as alternative chelators in agriculture.

Experimental

The determination of zinc in its ionic form was performed using differential pulse voltammetry (DPV) with a mercury electrode operating in Static Mercury Drop Electrode (SMDE) mode. The analysis was carried out with an AUTOLAB PGSTAT 12 potentiostat, equipped with GPES software and a 663 VA Stand mercury drop electrode. The experimental setup included a mercury working electrode, a silver chloride reference electrode, and a graphite auxiliary electrode. Measurements were conducted within a potential range of -1.2 V to -0.7 V, with a step size of 0.00495 V. Modulation amplitude was 0.00255 V and modulation time was 0.05 s. Equilibrium time was 5 s. The mercury drop size was set to 0.25 mm³.

The test samples were prepared by adding 2.0 cm³ of ZnSO_4 (0.001M), 2.0 cm³ of KCl (0.01M), 1.0 cm³ of gelatin solution (1%), and an appropriate amount of a chelator solution (0.001M) to achieve final molar ratios of 0.5:1, 1:1, and 2:1 relative to the zinc ions concentration. The list of the tested chelating agents is presented in Table 1, and their chemical structures are

presented in Fig. 1. Reference samples were also prepared without the addition of a chelating agent. The pH of the samples was adjusted to the desired level using NaOH and HCl solutions, and finally, the sample volume was 25 cm³.

Table 1

Full and abbreviated names of the studied organophosphorus compounds

Nitrilotris(methylenephosphonic acid)	NTMPA
Diethylenetriaminepenta(methylenephosphonic acid)	DETAPMPA
Ethylenediaminetetra(methylenephosphonic acid)	EDATMPA
1-Hydroxyethane-1,1-diphosphonic acid	HEDP
2-Phosphono-1,2,4-butanetricarboxylic acid	PBTCA

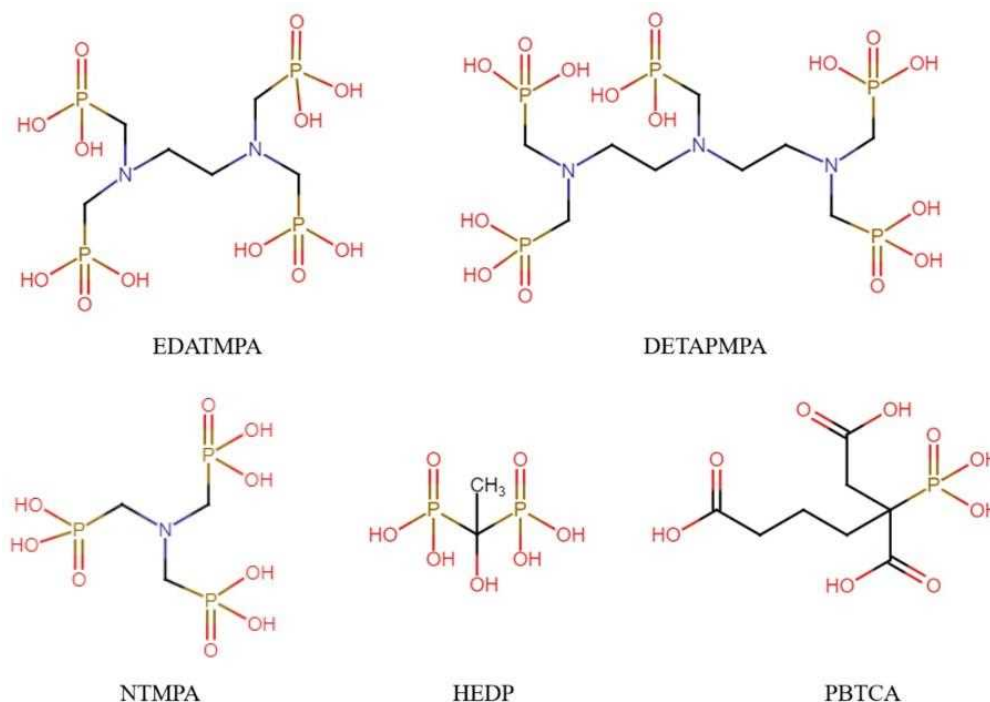


Fig.1. The structural formulas of the studied organophosphorus compounds.

The metal concentration is directly proportional to the intensity of the current signal. The degree of complexation was determined based on the difference between the metal ion concentration and the metal ion concentration in the presence of the chelating agent, according to Eq. (1).

$$\alpha = \frac{c_0 - c_i}{c_0} \cdot 100\% \quad (1)$$

where:

α – degree of Zn ions complexation [%],

c_0 – ions concentration of Zn before adding the chelator [mol/dm³],

c_i – ions concentration of Zn after adding the chelator [mol/dm³].

Results and discussion

The obtained results of zinc ions complexation degree by organophosphorus chelators, for the given pH values, are presented in Tables 2, 3, and 4.

At pH 3, the most effective chelator was EDATMPA, which achieved a zinc complexation degree of 78.1% at the highest concentration. NTMPA also performed well, yielding a similarly high result. In contrast, HEDP and PBTCA exhibited significantly lower complexation efficiencies, reaching 48.5% and 42.8%, respectively. The least effective chelator at this low pH was DETAPMPA, with a complexation degree of only 35.6% at a molar ratio of 1:2.

Table 2

Degree of zinc complexation [%] with different chelating agents at pH = 3

Molar ratio $C_{Zn^{2+}} : C_{\text{chelate}}$	NTMPA	EDATMPA	DETAPMPA	HEDP	PBTCA
1 : 0.5	41.8	51.4	24.7	39.7	37.1
1 : 1	42.8	54.9	32.5	47.4	38.1
1 : 2	74.1	78.1	35.6	48.5	42.8

Table 3

Degree of zinc complexation [%] with different chelating agents at pH = 5

Molar ratio $C_{Zn^{2+}} : C_{\text{chelate}}$	NTMPA	EDATMPA	DETAPMPA	HEDP	PBTCA
1 : 0.5	61.0	62.0	61.2	35.4	32.3
1 : 1	100.0	82.4	77.9	41.0	34.9
1 : 2	92.9	94.7	92.6	45.9	34.1

Table 4

Degree of zinc complexation [%] with different chelating agents at pH = 7

Molar ratio $C_{Zn^{2+}} : C_{\text{chelate}}$	NTMPA	EDATMPA	DETAPMPA	HEDP	PBTCA
1 : 0.5	46.9	71.6	89.7	40.8	12.1
1 : 1	89.5	93.4	98.8	48.8	13.6
1 : 2	99.3	99.0	99.5	60.4	20.7

At pH 5, NTMPA and EDATMPA once again demonstrated excellent zinc ion complexation, reaching 92.9% and 94.7%, respectively, at the highest tested concentration. However, DETAPMPA also demonstrated a high complexation degree of 92.6% at a molar ratio of 1:2. This suggests that DETAPMPA's chelating ability significantly improves at higher pH levels. HEDP exhibited similar performance to results at pH 3, indicating that its complexation capacity remains relatively stable across different pH conditions. In contrast, PBTCA showed a noticeable decline in complexation efficiency compared to pH 3, achieving only 34.1% at the highest tested concentration. This trend suggests that PBTCA's ability to bind zinc ions decreases as pH increases, making it less effective under neutral to slightly alkaline conditions.

At the highest tested pH, the complexation dynamics shift once again. At the highest examined molar ratio of chelator to zinc ions, NTMPA, EDATMPA, and DETAPMPA achieved nearly complete zinc complexation, with values close to 100%. HEDP, in comparison, reached a moderate complexation degree of zinc ions 60.4%. However, differences between the chelators become more apparent at lower molar ratios. At a M:L ratio – 1:1, NTMPA showed a complexation degree of zinc ions of 89.5%, while EDATMPA and DETAPMPA displayed significantly higher

values of 99.4% and 98.8%, respectively. The disparities become even more pronounced at a molar ratio of 1:0.5, where NTMPA, EDATMPA, and DETAPMPA achieved 46.9%, 71.6%, and 89.7%, respectively. PBTCA had much worse zinc ion complexing properties. At the appropriate molar ratio M:L, the degrees of complexation of the analyzed microelement ions were achieved equal to 12.1% at 1:0.5, 13.6% at 1:1, and 20.7% at 1:2. These results confirm that PBTCA has weak zinc-binding capabilities, particularly in higher pH environments, making it the least effective chelator among those studied.

Comparing the obtained results with literature data on aminopolycarboxylic acids (APCAs), particularly the findings presented by Borowiec et al. (2009) and Klem-Marciniak (2020), it can be concluded that the most effective organophosphorus chelators (NTMPA, DETAPMPA, and EDATMPA) exhibit complexation properties at higher pH values that are quite similar to those of commonly used APCAs [13, 14].

Despite the lower complexation efficiency observed at pH 3 compared to higher pH values, the results for organophosphorus chelators remain promising. The best-performing compounds, NTMPA and EDATMPA, still achieved notable zinc complexation, with values reaching nearly 80% at the highest tested molar ratio. These results indicate that, while organophosphorus chelators may be less effective in strongly acidic conditions than traditional APCAs, they still demonstrate significant potential for application in acidic environments.

Overall, while their performance is pH-dependent, the studied organophosphorus chelators show strong potential as zinc-binding agents. These initial results provide a foundation for further analyses of the properties of these substances, which represent a promising alternative to commonly used chelating agents. These initial results provide a foundation for further analyses of the properties of these substances, which represent a promising alternative to commonly used chelating agents.

Conclusions

The results indicate that generally the degree of zinc ion complexation increases with both rising pH and an increasing molar ratio of chelator concentration to zinc ion concentration. An exception to this rule is PBTCA, whose zinc complexation ability decreases as pH increases.

Among all the tested organophosphorus compounds, the best chelating properties were demonstrated by NTMPA, EDATMPA, and DETAPMPA. These compounds effectively complex zinc ions, indicating that the presence of at least one nitrogen atom in the molecular structure enhances their chelating ability.

The number of phosphonate groups in the chelator's structure also plays a significant role in its effectiveness. Compounds with a higher number of phosphonate groups show better chelating properties in higher pH environments.

When comparing the results obtained in this study with literature data on aminopolycarboxylic acids (APCAs), organophosphorus compounds like NTMPA, EDATMPA, and DETAPMPA exhibited chelation efficiency similar to commonly used APCAs, especially at higher pH values, which could make them a potential alternative with lower environmental toxicity.

Although the results at pH 3 were not as optimal as those at higher pH values, satisfactory zinc complexation was still achieved, suggesting that using higher molar ratios of chelator to metal could improve the effectiveness of these compounds at this pH.

The findings demonstrate that under specific conditions, certain organophosphorus chelators meet the requirements outlined in Regulation (EU) 2019/1009, which mandates a minimum of 80% complexation for chelating agents in micronutrient fertilizers. At higher pH values, NTMPA,

EDATMPA, and DETAPMPA successfully fulfilled this requirement at molar ratios of 1:1 and 1:2. At pH 3, NTPMA and EDATMPA were close to compliance at a molar ratio of 1:2, suggesting that a further increase in the molar ratio would be necessary to fully meet the regulatory criteria.

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Biocatalytic Method for the Synthesis of Enantiomerically Pure β -Methyl-phenylethylamines.

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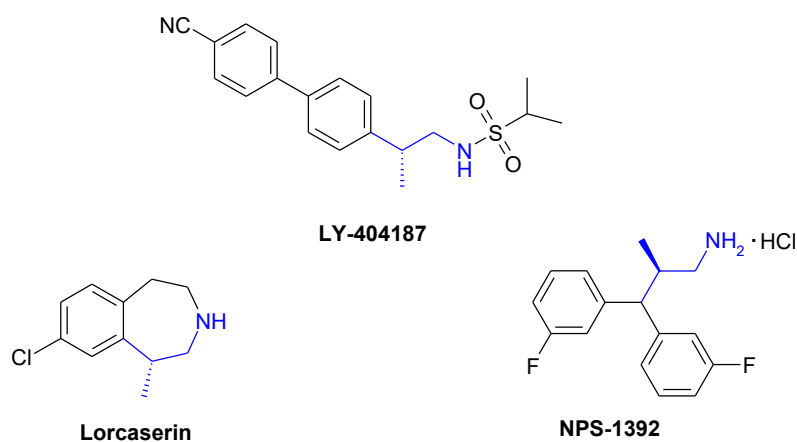
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Abstract. *A new method for the synthesis of important building blocks – enantiomerically pure β -methyl-phenylethylamines – has been developed. Kinetic dynamic enzymatic resolution methodology was applied at key stages of the synthesis. A double biocatalytic purification approach was used to achieve high optical purity of the obtained products. The resulting amines are promising building blocks for the development and production of new pharmaceuticals and biologically active compounds.*

Keywords: biocatalysis; chiral 3-arylbutanoic acids; chiral β -methyl phenylamines; lipase; enzymatic resolution, optical activity.

Introduction

Chiral amines are well-known key structural elements of both natural biologically active compounds and various pharmaceuticals [1-3]. Amines containing a β -methyl stereogenic center are present in many bioactive substances and medicinal drugs [4-6]. Among them are physiologically active compounds and pharmaceuticals such as Lorcaserin, a commercially available drug for obesity treatment, as well as biarylpropylsulfonamides and NPS-1392 – bioactive compounds that play a crucial role in the development of central nervous system disorders such as schizophrenia, autism, epilepsy, Parkinson's disease, Alzheimer's disease, and amyotrophic lateral sclerosis (Scheme 1) [4-6].



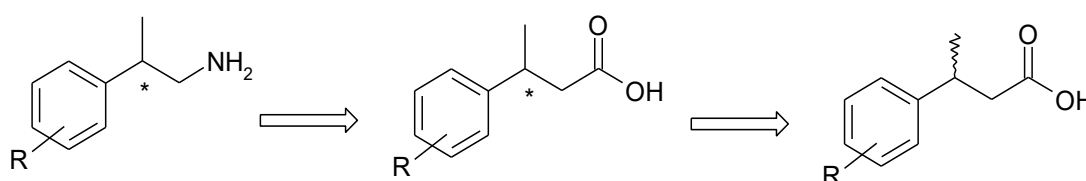
Scheme 1. Examples of pharmaceuticals and physiologically active compounds containing a β -methyl-ethylamine fragment.

In most cases, optically active β -methyl-phenylethylamine building blocks are obtained using asymmetric hydrogenation methods with Ru- and Rh-catalysts [7,8]. However, this method often has certain drawbacks, such as the high cost of these catalysts, the inability to obtain both enantiomers of the target compound, and the fact that these compounds are typically produced

only in small, milligram-scale quantities. Other methods explored for the synthesis of β -aryl-propylamines include chiral column separation, fractional crystallization, organocatalysis, and biocatalytic approaches. However, in all these cases, the enantioselectivity and chemical yields remained moderate [9-12].

Biocatalytic synthesis reactions are among the most economically advantageous transformations in synthetic organic chemistry, as the starting materials are usually produced on a large scale from inexpensive sources or are commercially available at a low cost. Another advantage of this method is the use of water as a solvent for these reactions. Water is one of the most environmentally friendly, inexpensive, and widely available solvents. Additionally, biocatalysts themselves are always of biological origin, derived from bacteria, fungi, or living cells. The conditions for enzymatic reactions are typically mild and environmentally friendly, making such approaches a key aspect of "green chemistry" [13].

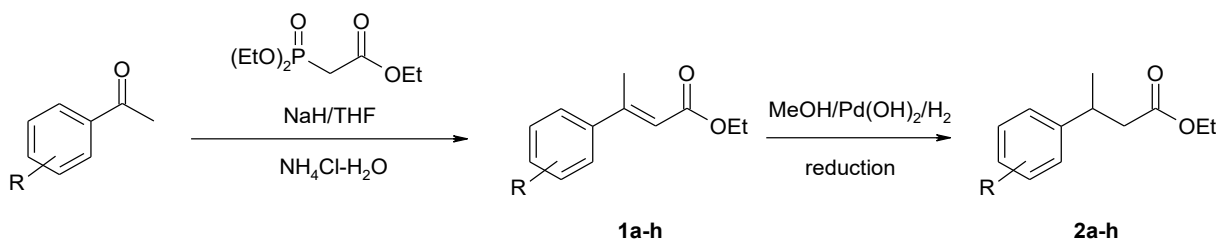
Thus, in our work, we employed this approach to obtain enantiomerically pure β -methyl-phenylethylamines. To achieve this goal, a multi-step synthetic scheme was developed, incorporating enzymatic hydrolysis of racemic 3-arylbutanoic acids at the key stage (Scheme 2).



Scheme 2. Retrosynthesis of β -methyl-phenylethylamines.

Results and discussion

Racemic esters of 3-arylbutanoic acids **2a–h** were synthesized using our previously reported method [14], following a two-step procedure outlined in Scheme 3 below.

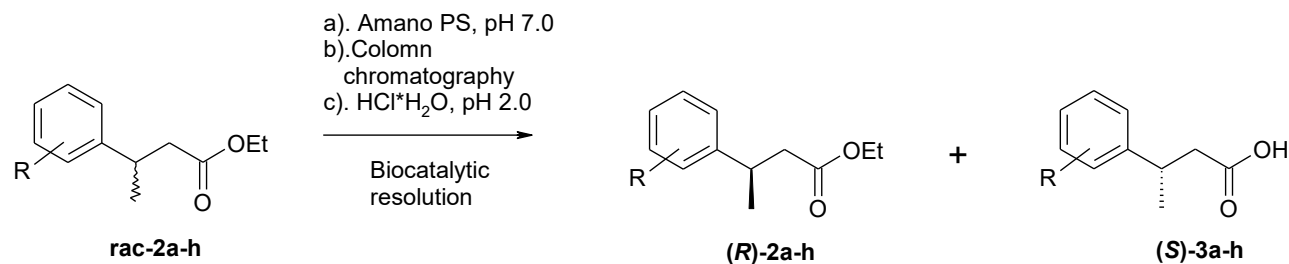


No	Compound	R
1	2a	H
2	2b	2-F
3	2c	4-F
4	2d	4-Br
5	2e	3-CF ₃
6	2f	4-Cl
7	2g	4-OMe
8	2h	4-CN

Scheme 3. Synthesis of racemic esters of 3-arylbutanoic acids.

In the first step of the synthesis, esters of unsaturated arylcarboxylic acids were obtained via the Horner–Wittig reaction, starting from the corresponding substituted acetophenones and ethyl 2-(diethoxyphosphoryl)acetate, followed by hydrogenation in the presence of palladium

hydroxide. As a result, ethyl 3-arylbutanoates **2a–h** were obtained with a 90% yield and were used in further transformations without additional purification.

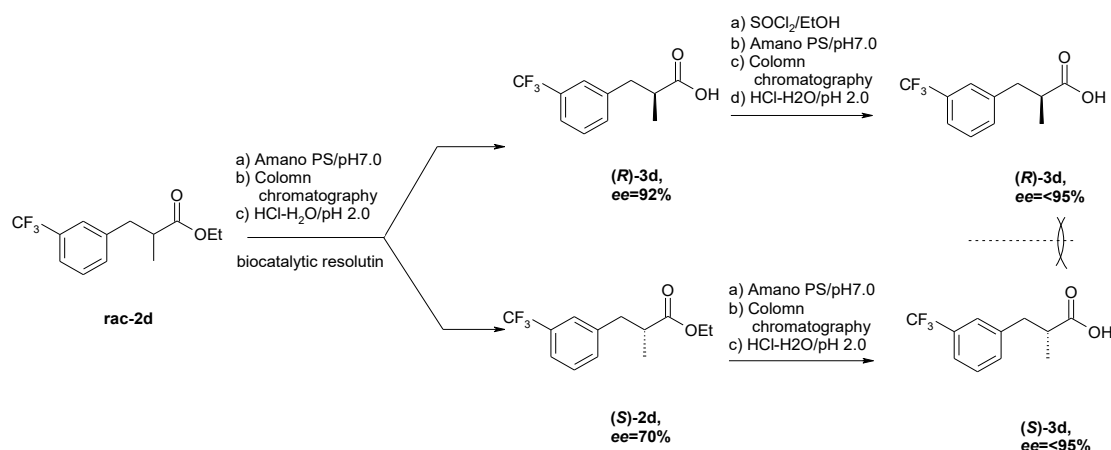


Compound	<i>(R)</i> -Ester			<i>(S)</i> -Acid		<i>E_a</i>
	R	Yield, %	ee, %	Yield, %	ee, %	
2a	H	45	91	41	90	>100
2b	2-F	48	95	27	77	>100
2c	4-F	45	95	47	94	>100
2d	4-Br	46	95	44	93	>100
2e	3-CF ₃	20	92	30	70	>100
2f	4-Cl	44	96	40	93	>100
2g	4-OMe	40	93	35	99	>100
2h	4-CN	41	92	42	99	>100

Scheme 4. Biocatalytic enantioselective resolution of arylcarboxylic acid esters

Next, the obtained racemic mixtures of esters were subjected to enzymatic kinetic resolution. Some of the most effective esterases and hydrolases were selected as biocatalysts, including lipases from *Burkholderia cepacia*, *Pseudomonas cepacia*, and *Candida antarctica* B, which combine broad substrate specificity with high regio- and enantioselectivity. The enzymatic hydrolysis of the racemic arylcarboxylic acid ester was carried out in a phosphate buffer at pH 7.0 using Amano PS lipase [14–16]. As a result, (*R*)- and (*S*)-arylcarboxylic acids **3a–g** were obtained with yields of 52–60% and enantiomeric purity of 77–99% (Scheme 4).

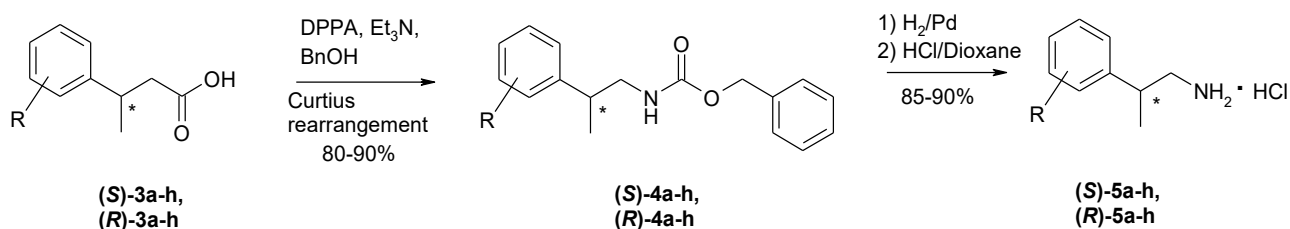
In cases of moderate optical purity of the obtained products, additional (double) enzymatic deracemization was employed to enhance the enantiomeric purity of the arylcarboxylic acids (Scheme 5) [14].



Scheme 5. An example of the double enzymatic deracemization of arylcarboxylic acids.

In the next stage of our work, the enantiomerically pure arylcarboxylic acids were converted into chiral, optically pure amines via the Curtius rearrangement, followed by hydrogenation of the intermediate Cbz-amines. All Cbz-amines **4a–g** were synthesized for the first time and characterized using ^1H NMR. They were used in subsequent reactions without further purification.

Thus, at the next stage, the Cbz-amines **4a–g** were subjected to hydrogenation in the presence of Pd/C (5%), followed by purification through recrystallization of the hydrochloride salts of the obtained amines. The reactions proceeded with good yields, resulting in the formation of the amine hydrochlorides **5a–g** (Scheme 6).



Scheme 6. Synthesis of β -methyl-phenylethylamines

The absolute configurations of the obtained products were determined by comparing the optical rotation values with literature data. It was thus shown that all the amines were obtained with retention of the absolute configuration of the stereogenic center. All optically active β -methyl-phenylethylamines were obtained with high chemical yields, optical purity $>95\%$, and with retention of the absolute configuration of the chiral center. They were described and characterized using modern physicochemical methods, such as NMR, HPLC, LC-MS, elemental analysis, and optical rotation measurements.

Conclusion

In this work, we have obtained and described all the optical isomers of β -methyl-phenylpropanoic acids. For this, we applied the methodology of enzymatic kinetic resolution using various lipases, such as *Burkholderia cepacia* lipase, *Pseudomonas cepacia* lipase, and *Candida antarctica* B lipase. The best and most efficient lipase for the enzymatic hydrolysis of β -methyl-phenylpropanoic acids, Amano PS lipase, was identified. To achieve the highest level of enantiomeric purity, a dual biocatalytic deracemization method was applied. Subsequently, the obtained β -methyl-phenylpropanoic acids were converted into optically pure β -methyl-phenylethylamines, with the Curtius rearrangement used at the key stage. All optically active β -methyl-phenylethylamines were obtained with high chemical yields, optical purity $>95\%$, and retention of the absolute configuration of the chiral center, and were described and characterized using modern physicochemical methods. Thus, all the enantiomers of β -methyl-phenylethylamines were obtained, which represent promising building blocks for the synthesis of potential pharmaceuticals and biologically active compounds.

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Enhancing Mechanical Properties of Biopolymer-Based Composites: The Influence of Organic and Inorganic Additives

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Abstract. *This study investigates the mechanical properties of modified biopolymer-based composites reinforced with organic (collagen, keratin) and inorganic (silicates, cellulose derivatives) additives. Results demonstrate enhanced tensile strength and elongation at break, highlighting the potential of optimized additive concentrations for improving bioplastic durability. These findings contribute to the development of sustainable, high-performance biodegradable materials.*

Keywords: biopolymers, biodegradable materials, mechanical properties, biocomposites, sustainable plastics, polymer additives, material reinforcement, eco-friendly materials.

Introduction

The widespread use of petrochemical-based plastics has significantly contributed to environmental degradation, leading to growing concerns regarding pollution, resource depletion, and long-term sustainability [1, 2]. Conventional plastics, such as polyethylene (PE), polypropylene (PP), polystyrene (PS), and polyethylene terephthalate (PET), are extensively utilized across various industries due to their excellent mechanical properties, chemical resistance, durability, and cost-effectiveness [3]. These materials have revolutionized modern manufacturing, enabling advancements in packaging, construction, automotive, medical devices, and consumer goods. However, despite their functional advantages, the persistence of synthetic polymers in the environment presents severe ecological and health challenges [4].

Non-biodegradable plastic waste accumulates in landfills, oceans, and natural ecosystems at an alarming rate. Global plastic production exceeds 300 million metric tons annually, with a substantial fraction ending up as unmanaged waste [5]. Microplastic contamination in aquatic and terrestrial environments has been identified as a critical issue, posing risks to marine biodiversity, food chains, and human health. Furthermore, the extraction and processing of fossil fuels for plastic production contribute significantly to greenhouse gas emissions, exacerbating climate change [6]. The long-term consequences of plastic pollution have led to increasing regulatory pressures, public awareness, and scientific initiatives aimed at developing sustainable alternatives that maintain material performance while minimizing environmental impact [7].

Biopolymers have emerged as promising candidates for reducing plastic-related pollution due to their renewable origin and potential biodegradability [8]. These materials are derived from various natural sources, including polysaccharides, proteins, and polyesters, making them an environmentally friendly alternative to petroleum-based polymers [9]. Polysaccharides such as cellulose, starch, chitosan, and agar-agar are among the most abundant and widely studied biopolymers, offering excellent biodegradability and renewability [10]. Their hydrophilic nature and ability to form strong hydrogen bonds contribute to desirable properties such as film-forming capabilities and biocompatibility. However, their mechanical strength, moisture sensitivity, and barrier properties often require further enhancement through chemical modifications or blending with other materials [11].

Proteins, including collagen, keratin, casein, and gelatin, are another class of biopolymers that have gained attention for their unique structural properties [12]. These macromolecules are

naturally designed to provide mechanical support in biological systems, making them suitable candidates for biopolymer applications. Collagen, the primary structural protein in connective tissues, exhibits excellent tensile strength and flexibility, making it particularly useful for biomedical applications such as wound dressings, scaffolds for tissue engineering, and drug delivery systems [13]. Similarly, keratin, which is found in hair, feathers, and wool, is known for its high sulfur content and disulfide bond crosslinking, leading to increased strength and stability [14]. Casein, the primary protein in milk, has been explored for its ability to form films with moderate strength and elasticity, offering potential applications in biodegradable packaging. Despite their advantages, protein-based biopolymers often suffer from water sensitivity, limited thermal stability, and relatively low mechanical strength, necessitating reinforcement through additives or chemical modifications [15].

In addition to polysaccharides and proteins, biopolyesters such as polylactic acid (PLA) and polyhydroxyalkanoates (PHA) have gained prominence due to their thermoplastic nature and processability [16]. PLA, derived from lactic acid fermentation of plant-based sugars, has mechanical properties comparable to polystyrene and polyethylene terephthalate (PET), making it a popular choice for biodegradable packaging, medical implants, and 3D printing [17]. However, its brittleness and low impact resistance require blending with plasticizers or other biopolymers to improve flexibility. PHA, a family of microbial polyesters produced by bacterial fermentation, offers superior biodegradability and biocompatibility, making it suitable for biomedical and agricultural applications [18]. The diversity of PHA copolymers allows for tunable mechanical and thermal properties, but high production costs remain a significant barrier to large-scale commercialization [19].

Despite their environmental benefits, biopolymers face significant challenges that hinder their widespread adoption in high-performance industries such as packaging, automotive, aerospace, and biomedical fields [20]. One of the primary limitations is their inferior mechanical properties compared to traditional synthetic polymers. Many biopolymers exhibit lower tensile strength, increased brittleness, and limited thermal stability, restricting their application in demanding environments [21]. These weaknesses are particularly problematic for applications requiring high durability, flexibility, or resistance to external factors such as moisture, UV radiation, and mechanical stress [22].

To overcome these challenges, researchers have explored various strategies to enhance the mechanical performance of biopolymer-based materials. These strategies include blending biopolymers with synthetic or natural reinforcements, crosslinking polymer chains, plasticization, and composite formulation with inorganic additives [23]. The incorporation of organic additives such as collagen, keratin, and casein has been shown to improve elasticity and toughness, while inorganic reinforcements such as silicates, calcium phosphates, and cellulose nanocrystals enhance structural rigidity and impact resistance. Furthermore, functionalized nanoparticles and bioactive fillers can introduce additional properties such as antimicrobial activity, UV resistance, and improved barrier performance [24].

Given the increasing demand for sustainable materials, ongoing research efforts focus on optimizing the formulation and processing of biopolymer composites to achieve a balance between mechanical performance, biodegradability, and cost-effectiveness [25]. The development of multi-component biopolymer composites that combine the advantages of different biopolymers and reinforcement materials holds great promise for advancing sustainable plastics and reducing environmental impact. This study aims to investigate the mechanical behavior of modified biopolymer-based composites reinforced with organic and inorganic additives. By analyzing

tensile strength and elongation at break, this research seeks to identify the most effective additive compositions that improve the durability and functionality of biodegradable materials. The findings of this study contribute to the ongoing development of high-performance, environmentally friendly bioplastics, offering potential applications in sustainable packaging, biomedical engineering, and structural materials.

Results and Discussion

The mechanical properties of the modified biopolymer composites were evaluated based on tensile strength (TS) and elongation at break (Eb), providing insights into the effects of different organic and inorganic additives on material performance. The results demonstrated significant variations depending on the type and concentration of the additives, with certain compounds substantially enhancing the mechanical stability of the material, while others exhibited a negative impact when used in excessive amounts.

In terms of tensile strength, the most significant improvement was observed in the sample containing 0.1 g of agar-agar, which exhibited a tensile strength 21% higher than the strongest non-modified biopolymer sample. This increase is likely attributed to agar-agar's ability to enhance interfacial adhesion within the biopolymer matrix, promoting stronger intermolecular interactions. Cellulose acetate at 1 g also exhibited a noticeable reinforcing effect, increasing tensile strength by 15% compared to the base material. Similarly, collagen type II at 2 g demonstrated a 12% improvement, reinforcing the role of protein-based additives in enhancing mechanical robustness. The 0.5 g ortho-silicate sample resulted in a 10% improvement in tensile strength relative to the non-reinforced control, which aligns with previous studies indicating the potential of silicate-based reinforcements in stabilizing polymer networks.

Conversely, certain additives at higher concentrations led to a deterioration in mechanical properties. For instance, increasing the concentration of collagen type II from 2 g to 3 g resulted in a 7% decrease in tensile strength, likely due to phase separation and reduced homogeneity of the composite structure. A similar trend was observed for cellulose acetate, where increasing its content beyond 1 g caused a 9% reduction in tensile strength, indicating that excessive filler content may disrupt the polymer matrix and lead to stress concentration points. These findings suggest that while moderate concentrations of certain additives can enhance material performance, exceeding the optimal threshold can have the opposite effect.

Regarding elongation at break, which measures the material's flexibility and ductility, Aerosil (0.5 g) exhibited the most pronounced improvement, increasing Eb by 48% relative to the control sample. This suggests that nanoscale dispersion of silica enhances polymer chain mobility, reducing brittleness and improving flexibility. Similarly, 3-aminopropyltriethoxysilane (1 g) contributed to an elongation increase of 32%, reinforcing the role of silane coupling agents in promoting plasticity within biopolymer matrices. Another notable improvement was seen in collagen type III (0.5 g), which improved elongation at break by 27%, likely due to the inherent elasticity of collagen fibers, which facilitate stress distribution across the polymer network.

Interestingly, while some organic fillers improved flexibility, others had a stiffening effect when used in high concentrations. For example, increasing hydrolyzed keratin content from 2 g to 4 g resulted in a 15% decrease in elongation at break, indicating that excessive protein reinforcement leads to a more brittle material. Likewise, high concentrations of cellulose acetate (above 1 g) reduced elongation by 18%, suggesting that an overly rigid polymer network compromises material ductility. These observations emphasize the importance of balancing reinforcement and flexibility to optimize composite properties for specific applications.

Overall, the results indicate that the mechanical performance of biopolymer-based composites is highly dependent on additive type and concentration. Moderate amounts of organic fillers such as collagen and keratin contribute to enhanced elasticity and durability, while inorganic reinforcements like silica-based additives improve tensile strength without sacrificing flexibility. However, excessive filler content can lead to phase separation, decreased homogeneity, and the formation of brittle domains, ultimately reducing material performance. These findings highlight the potential for fine-tuning biopolymer formulations to achieve a balance between strength, flexibility, and biodegradability, paving the way for improved applications in sustainable packaging, biomedical engineering, and structural materials. Future research should focus on refining processing techniques and exploring synergistic additive interactions to further enhance the mechanical properties of biopolymer-based materials.

Conclusions

The results of this study demonstrate that the mechanical properties of biopolymer-based composites can be significantly enhanced through the careful selection and optimization of organic and inorganic additives. The findings indicate that moderate concentrations of agar-agar, cellulose acetate, and collagen type II contribute to improved tensile strength, increasing it by up to 21% compared to the non-reinforced material, while maintaining structural integrity. Similarly, Aerosil and 3-aminopropyltriethoxysilane were the most effective in increasing elongation at break, enhancing flexibility by 48% and 32%, respectively. However, excessive additive concentrations resulted in material degradation, reducing mechanical stability and leading to phase separation and increased brittleness. This underlines the necessity of optimizing filler content to balance strength, elasticity, and processability for specific applications. These insights are crucial for the advancement of sustainable biopolymer formulations, allowing for the development of high-performance biodegradable materials with tailored mechanical properties. Future work should explore long-term durability, environmental degradation behavior, and potential industrial applications to further enhance the practical viability of these composites in packaging, biomedical engineering, and structural applications.

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Organs-on-a-chip in the Study of Ophthalmic Diseases

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Abstract. *Recent advances in organ-on-chip technology provide innovative platforms for studying ophthalmic diseases. These microphysiological systems mimic the complex in vivo microenvironment, enabling more precise disease modeling and drug testing. This paper reviews the latest developments in corneal and retinal organ-on-chip models, highlighting their potential to revolutionize ophthalmic research and personalized medicine.*

Keywords: organ-on-chip, ophthalmology, microphysiological systems, corneal models, retinal models, disease modeling, drug testing, tissue engineering, *in vitro* platforms, personalized medicine.

Introduction

According to estimates [1], there are over 217 million people worldwide with moderate to severe visual impairment, including 36 million who are blind. The leading irreversible causes of vision loss include cataracts, glaucoma, age-related macular degeneration, corneal opacities, and diabetic retinopathy [2, 3]. These conditions significantly affect quality of life and are becoming increasingly relevant in aging populations. To better understand the underlying mechanisms of ocular pathologies and develop novel therapeutic approaches, advanced models capable of accurately replicating the structure and function of the eye are required.

Currently, various models are used to study ocular diseases, including *in silico* approaches, animal models, *ex vivo* explant cultures, traditional 2D cell cultures, and 3D organoids. While these systems are valuable for specific research applications and can complement each other, none fully recapitulate the complex architecture and functional properties of the human eye. Moreover, most of them have significant limitations, such as high costs, limited availability, reproducibility challenges, and ethical concerns.

Advances in stem cell technologies and microengineering have led to the development of microphysiological systems and organ-on-chip (OoC) platforms. This innovative technology integrates human tissues into microfluidic devices that mimic the natural *in vivo* microenvironment [4]. Ophthalmic OoC models have the potential to overcome the major drawbacks of existing systems, offering new opportunities for studying ocular diseases and developing effective treatments. This paper reviews the current ophthalmic OoC systems and their future prospects.

The aim of the work was to analyze the latest trends and outline the direction and focus of further work, reviewing the latest developments in the new field of organs on a chip, with an emphasis on the use of chips in the study of ophthalmic diseases. The paper is review-based and does not include laboratory experiments.

I Eye anatomy

The eye is composed of multiple structurally and functionally distinct tissues that contribute to its optical, sensory, and protective functions. Its key components can be categorized into anterior and posterior structures.

The cornea, a transparent outer layer, plays a crucial role in refracting light and directing it toward the internal ocular structures. It consists of a multilayered epithelium, stroma, basement

membrane, Dua's layer, Descemet's membrane, and endothelium. The cornea's transparency is maintained through the unique organization of collagen fibers and the absence of blood vessels. A tear film covering the corneal surface serves as a protective barrier and influences the bioavailability of ophthalmic drugs [5].

The lens is a flexible, biconvex structure responsible for fine-tuning light focus onto the retina, working in conjunction with the cornea. Its transparency is preserved by specialized proteins called crystallins. Surrounding the lens, the ciliary body regulates accommodation and produces aqueous humor, which circulates between the anterior and posterior chambers of the eye. This fluid plays a critical role in maintaining intraocular pressure, and disruptions in its regulation can contribute to the development of glaucoma [6].

The retina is a highly specialized light-sensitive tissue composed of photoreceptors (rods and cones), bipolar neurons, and ganglion cells. It converts incoming light signals into neural impulses, which are transmitted to the brain via the optic nerve. The retinal pigment epithelium (RPE) supports photoreceptor function by performing critical tasks such as phagocytosis of outer segment discs and forming the outer blood-retinal barrier. Degeneration of the RPE is a key factor in the pathogenesis of age-related macular degeneration (AMD) [7].

The choroid, particularly the choriocapillaris, provides essential nutrients to the outer retinal layers. The blood-retinal barrier (BRB) consists of two components: the inner BRB, formed by tight junctions between retinal capillary endothelial cells, and the outer BRB, composed of the RPE, which regulates metabolic exchange between the choroidal vasculature and photoreceptors [6].

Disruptions in the blood-retinal barrier are a major pathogenic mechanism in diabetic retinopathy and other retinal diseases.

II Cornea-on-a-Chip

Cornea-on-a-chip engineering remains in its early stages of development. Despite the relative simplicity of the cornea compared to other ocular structures, existing corneal chip models have already demonstrated the ability to replicate certain disease-specific characteristics. The initial attempts at culturing corneal cells in microfluidic systems involved a two-layer design consisting of an epithelial layer and a stromal cell layer embedded in a collagen-based hydrogel. This model was primarily used to assess transepithelial permeability [8].

Nearly a decade later, Bennet et al. developed a corneal-on-a-chip platform that incorporated epithelial layers, a basement membrane, and Bowman's membrane while also simulating tear flow dynamics within a microfluidic environment [9]. Their approach utilized immortalized human corneal epithelial cells (hTCEpi) cultured on a polydimethylsiloxane (PDMS) membrane. Notably, cells seeded onto fibronectin-coated membranes exhibited greater viability than those grown on uncoated or collagen-coated surfaces. Furthermore, under flow conditions, epithelial permeability closely resembled in vivo characteristics.

A major breakthrough in ocular surface modeling came with the work of Seo et al., who designed an integrated platform combining corneal and conjunctival structures with a blinking eyelid model [10]. Their design featured a dome-shaped scaffold with a perfusion system and a moving eyelid-like component that slid across the surface. The corneal model included epithelial cells layered over primary human keratocytes encapsulated in a hydrogel to mimic the stroma. Using 3D patterning techniques, they fabricated concentric conjunctival and corneal structures containing epithelial and goblet cells. However, this model lacked vascular networks and immune cells, which are naturally present in the conjunctiva in vivo.

Seo and colleagues further refined their ocular chip, successfully replicating key anatomical and physiological aspects of the human eye [10]. The stratified epithelium of their system consisted of 7–8 layers of epithelial cells, closely resembling the native corneal structure. Additionally, a subset of basal cells expressed the p63 marker, indicative of their proliferative potential. Similarly, the engineered conjunctiva exhibited multilayered epithelium and expressed key biochemical markers. A particularly significant feature was the production of mucin proteins, an essential function of the conjunctiva.

One of the most innovative aspects of this model was its integration of biomechanical processes, including physiological blinking frequency (0.2 Hz) and tear film dynamics. The tear secretion rate was meticulously calibrated to match physiological conditions, with an integrated drainage system to remove excess fluid. As a result, the device was capable of maintaining a thin and uniform tear film ($\sim 6 \mu\text{m}$), a feature confirmed through optical coherence tomography. Importantly, the blinking mechanism did not cause ocular surface damage or scarring. Moreover, mechanical shear stress promoted epithelial cell differentiation, suggesting that the eyelid plays not only a protective role but also contributes to mechanotransduction via biochemical signaling pathways.

While ocular chips have yet to be fully optimized for disease modeling, a significant milestone in this direction was the development of a dry eye disease (DED) model [10]. To simulate DED conditions, the system was adjusted to reduce the blinking frequency from 12 to 6 times per minute while modifying environmental humidity levels. These changes led to increased tear film osmolarity and instability, as indicated by reduced tear breakup time. Notably, these biomechanical alterations triggered cellular responses similar to those observed in DED patients *in vivo*. For instance, a decrease in blinking frequency resulted in upregulated expression of proinflammatory cytokines, including interleukin-1 β (IL-1 β), tumor necrosis factor- α (TNF α), and matrix metalloproteinase-9 (MMP-9).

III Retina-on-a-Chip

Retinal tissue regeneration through cell transplantation represents another crucial area in the development of ophthalmic chip technology. In cell-based therapies, degenerating retinal cells are replaced by injecting retinal precursor cells. However, this approach remains highly challenging, as the success of transplantation depends on factors such as the migration, maturation, and integration of implanted cells with the host retina [11]. A key limitation is the relatively low number of viable transplanted cells that successfully migrate into the damaged retinal tissue. In this context, the optical accessibility and transparency of model systems are critical, as real-time observations are not feasible in *in vivo* models [12]. As a result, research teams have focused on developing retina-on-a-chip platforms to study the behavior of transplanted cells.

One such advancement was the development of a microfluidic chip designed to investigate retinal synapse regeneration, known as the RSR-chip (retinal synaptic regeneration chip), by Su and colleagues [11]. This device featured two microchambers connected by an array of microchannels. Retinal precursor cells derived from mice were seeded separately into each chamber. After three days, axons from one cell population began extending toward the other. In response to cytokine secretion, synaptic regeneration was observed within the RSR-chip. Moreover, the formation of an organized synaptic network was detected, and an automated system facilitated the quantification of synaptic connectivity. To validate the functionality of the chip, researchers tested its response to different concentrations of glycine, a known inhibitory neurotransmitter in the retina. Additionally, retinal electrophysiological activity was assessed using immunodetection of phosphorylated ERK (pERK), a kinase linked to extracellular signal

regulation. The primary goal of this chip was to explore synaptogenesis mechanisms and screen factors that promote retinal regeneration.

In the same year, another innovation emerged with the introduction of the μ Retina chip, designed to mimic both mouse and human retinal structures [12]. Two distinct models were developed, each incorporating design parameters tailored to the specific characteristics of the human and murine retina. The human μ Retina consisted of three compartments interconnected by microchannels. Two rounded chambers positioned at the top and bottom functioned as reservoirs, while the central arc-shaped chamber replicated the curvature of the retina. The mouse μ Retina followed a similar design but was adapted to match the structural parameters of the murine retina. Retinal progenitor cells from mice were seeded into the arc-shaped compartment of the device, with the main objective being the study of cell migration patterns to refine transplantation strategies for retinal degenerative diseases. The viability of these cells was evaluated by exposing them to varying concentrations of stromal cell-derived factor-1 (SDF-1), a well-established chemoattractant for central nervous system cells. High concentrations of SDF-1 induced directed cell movement along the gradient, whereas lower concentrations failed to elicit significant migration.

A different approach was employed by Dodson and colleagues, who introduced a platform (Fig. 1) specifically designed for localized analysis of retinal tissue explants [13]. This system enabled the long-term culture of murine retinal explants, including resident microglial cells. Since retinal explants are naturally rounded, the device incorporated suction channels to ensure proper alignment, which was essential for high-resolution microscopic imaging. Additionally, the chip featured 12 independent channels, allowing for localized delivery of various substances, such as pharmaceutical compounds or signaling molecules.

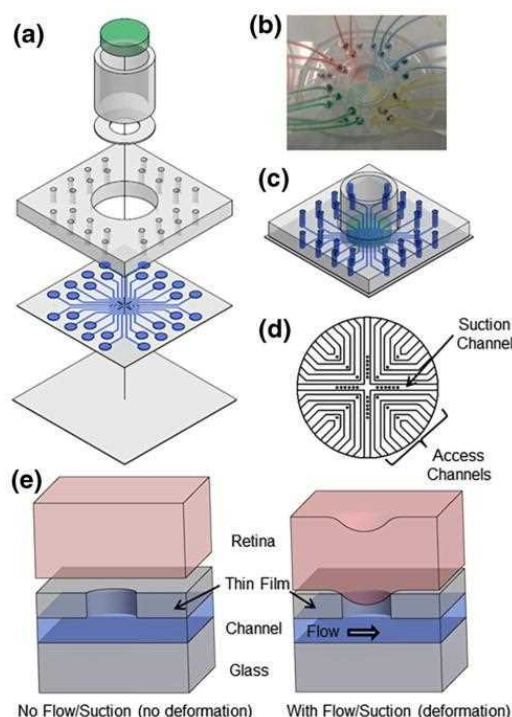


Fig. 1. Microfluidic retina-on-a-chip platform: (a) projection of the retina reservoir, agarose gel (green), and glass cylinder; (b) top view of the fluid flow without the medium cylinder; (c) assembly view with filled channels. (d) Enlarged diagram showing the arrangement of available and suction channels (width – 300 μ m, holes – 100 μ m). (e) Retina deformation: without flow, the tissue remains stationary; under negative pressure, it seals the holes, controlling the fluid flow [13].

The platform maintained tissue viability for 5 days. To assess its ability to model inflammation, the explants were exposed to lipopolysaccharide, followed by evaluation of microglial activation.

By using induced pluripotent stem cells and microfluidic systems, the retina-on-a-chip provides a controlled microenvironment for cells, simulating the natural flow of nutrients and oxygen [14]. This enables researchers to study disease mechanisms in greater detail and test new drugs under physiologically relevant conditions. These models have already demonstrated effectiveness in reproducing the barrier properties of retinal pigment epithelium, forming vascular networks, and recording electrophysiological activity of cells.

The authors emphasize [14] that the next step in the development of retina-on-a-chip should involve improving cellular maturity and integrating more complex tissue components. This will allow the creation of individualized disease models for personalized medicine and significantly expand the possibilities for pharmacological screening.

IV Further research

The future development of organ-on-a-chip technologies in ophthalmology should focus on integrating several critical areas to enhance model functionality, better replicate in vivo conditions, and ensure high clinical relevance.

One of the most promising directions involves the incorporation of vascular networks and immune cells into ocular chip models. This is essential for simulating inflammatory and vascular processes characteristic of diseases such as diabetic retinopathy, uveitis, and dry eye disease. Creating dynamic interactions between vascular endothelium and immune cells, including macrophages and microglia, will significantly improve the biological realism of the models.

Most current systems are designed for short-term use or to study acute responses. However, chronic conditions such as glaucoma, age-related macular degeneration (AMD), or chronic dry eye require long-term and stable platforms that allow continuous observation of disease progression. Future efforts should focus on adapting microfluidic systems for prolonged culture and fine control of the microenvironment over several weeks.

A key strategic direction is the development of personalized organ-on-a-chip models using iPSCs derived from individual patients. These models will allow researchers to study disease mechanisms in the context of specific genetic backgrounds and enable personalized drug testing tailored to individual patient responses.

For broader implementation in preclinical research, it is essential to establish standardized designs and protocols for ocular chips. At the same time, these platforms should be scalable, supporting high-throughput drug screening and facilitating their integration into pharmaceutical development pipelines.

Conclusions

The organ-on-a-chip technology opens up new possibilities for ophthalmological research, providing precise replication of physiological and pathological processes in in vitro conditions. Corneal and retinal microphysiological systems enable the modeling of eye diseases, testing of drugs, and evaluation of the effectiveness of cell therapy, reducing dependence on traditional models such as animal experiments.

Despite significant progress, further research is needed to refine bioengineering techniques, integrate vascular and neural components, and enhance the potential of personalized medicine. One of the key priorities is the incorporation of vascular and immune elements into ocular chip platforms, which will enable more accurate simulation of inflammatory and vascular conditions

such as diabetic retinopathy and uveitis. Equally important is the development of stable and durable systems capable of long-term culture, as chronic diseases like glaucoma and age-related macular degeneration require extended observation of tissue behavior over time. Furthermore, the use of induced pluripotent stem cells (iPSCs) for generating patient-specific models holds great promise, as it allows for individualized disease modeling and drug response evaluation, ultimately laying the groundwork for personalized therapeutic strategies.

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Enzymatic Synthesis is a Method for Obtaining Optically Active Compounds.

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Abstract. *Enzymatic synthesis is one of the most fascinating topics in asymmetric catalysis. This method is one of the most efficient, widely applied, and, in many cases, universal for the resolution of racemic mixtures. It allows for producing various organic compounds in enantiomerically pure form relatively easily under mild conditions and with quantitative yields.*

Keywords: biocatalysis, lipase, enzymatic resolution, optical activity, enantiomerically pure compounds.

Introduction

Symmetry is an inherent property of living organisms. Asymmetric carbon atoms create chirality in molecules – the ability to exist in two mirror-image forms. Almost all chiral molecules in living organisms exist in only one form: sugars are exclusively dextrorotatory, amino acids are levorotatory, and DNA forms right-handed helices. The presence of carbon atoms with four chemically distinct substituents leads to the formation of chiral molecules with fixed mirror-image forms, known as stereoisomers. Symmetry is a fundamental aspect of nature, and many important scientific problems depend on understanding the reasons for the presence or absence of symmetry and asymmetry.

In recent years, the demand for chiral pharmaceutical agents has significantly increased. Guidelines on this issue were published by the U.S. Food and Drug Administration (FDA) as early as 1992 in a document titled "Development of New Stereoisomeric Drugs" [1, 2]. According to these guidelines, if a new pharmaceutical drug contains one or more chiral centers in its structure, all possible stereoisomers of the substance must be obtained in pure form, described, and tested. As a result, the demand for enantiomerically pure drugs is growing annually by 13–15% [3, 4]. Therefore, the search for and development of new methods that enable the production of all possible isomers of new compounds in optically pure form is a relevant and important task in modern bioorganic and pharmaceutical chemistry.

Enzymatic deracemization has attracted particular interest as a simple and efficient approach for synthesizing enantiomerically pure pharmaceutical agents. This methodology offers numerous advantages, including high enantioselectivity, versatility, mild reaction conditions, high chemical, regio-, and stereospecificity, environmental friendliness, quantitative product yields, methodological simplicity, and scalability [5]. Thus, enzymatic deracemization is an excellent method for obtaining optically pure precursors for the synthesis of novel pharmaceuticals and for achieving a "chiral switch" – a pharmaceutical chemistry strategy that involves transitioning from a racemic drug to its enantiomerically pure form [6].

Results and discussion

Enzymatic synthesis is a method for obtaining enantiomerically pure organic compounds using enzymes as biocatalysts. This approach leverages the high stereoselectivity of enzymes to selectively convert one enantiomer in a racemic mixture, ensuring an environmentally friendly process with mild reaction conditions and high efficiency. Various types of biocatalysts are employed for these transformations, including native lipases, immobilized lipases, and even whole-cell cultures of microorganisms (fungi, bacteria).

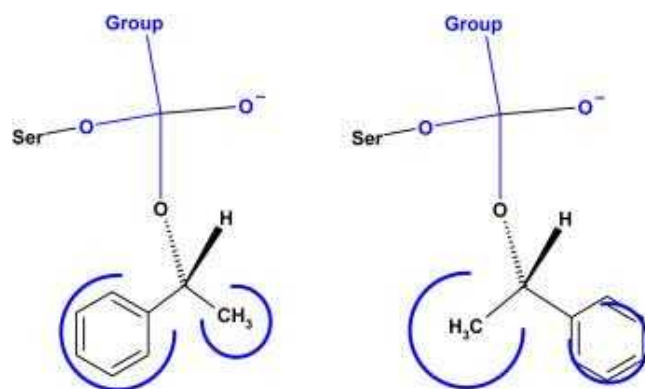
The most convenient enzymes for stereoselective organic synthesis are immobilized enzymes on various carriers such as silica gel, ceramics, and Celite. Immobilized enzymes offer

numerous advantages, including enhanced enzyme stability, reusability, improved selectivity and activity, ease of handling and product purification, controlled reaction conditions, higher process efficiency, and environmental sustainability.

Enzymes commonly used for the enzymatic kinetic resolution of racemic mixtures include lipases, hydrolases, amidases, and esterases. These enzymes enable the resolution of a wide range of chiral organic compounds, including primary, secondary, and tertiary alcohols; amines; α - and β -amino acids and their esters; hydroxycarboxylic and alkylcarboxylic acids and their esters; aryl- and heteryl-cycloalkyl alcohols and amines; as well as halogen-containing, organophosphorus, and fluorogenic compounds.

In the vast majority of cases, the resolution of these compounds follows Kazlauskas' rule. Kazlauskas' rule is an empirical guideline that helps predict which enantiomer of a racemic substrate will undergo hydrolysis or transformation by a lipase or another enzyme during kinetic or dynamic kinetic resolution. It is based on the priorities of substituents according to the Cahn–Ingold–Prelog (CIP) nomenclature and states that acylation (esterification) reactions predominantly occur with the *pro-R* enantiomer, while ester hydrolysis reactions primarily take place with the *pro-S* enantiomer (Scheme 1).

Thus, Kazlauskas' rule is widely used for the resolution of racemic secondary alcohols in pharmaceutical chemistry and, in most cases, accurately predicts the absolute configuration of enzymatic resolution products, which is crucial for obtaining enantiomerically pure drugs [7].

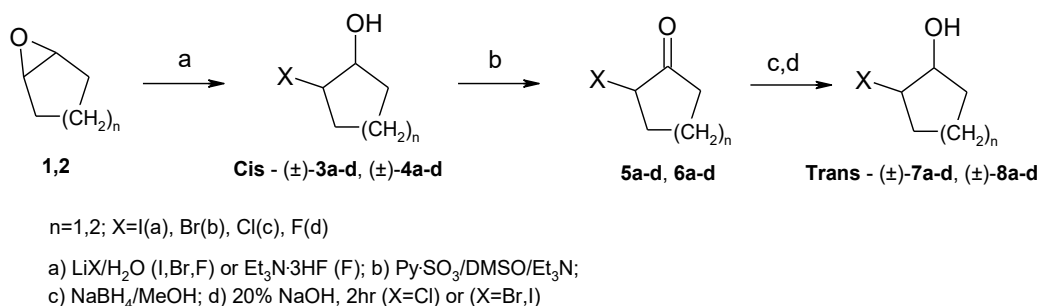


Scheme 1. Kazlauskas' rule.

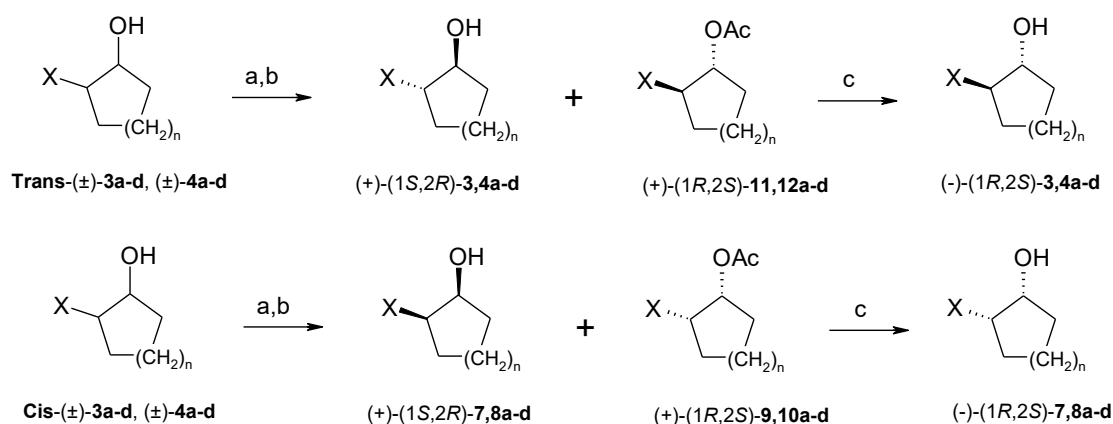
In our laboratory, we are working on developing new methods and approaches for the enzymatic resolution of various chiral organic compounds and obtaining these compounds in optically pure form. Due to the fact that the biocatalytic synthesis method for enantiomerically pure substances is quite versatile on the one hand and simple and highly stereospecific on the other, we work with a wide range of different classes of organic compounds in our research.

Vicinal halogeno-cycloalkanol derivatives are common building blocks for a number of chiral natural and synthetic products. These compounds are important reagents for organic synthesis and are widely used for the preparation of various biologically active compounds, in particular, prostaglandins and leukotriene precursors. Using this methodology, all possible stereoisomers of halogenated cyclopentanol and halogenated cyclohexanol derivatives were obtained. First, racemic *cis*- and *trans*-halogenated cycloalkanols (Scheme 2) were synthesized, which were then subjected to enzymatic resolution with vinyl acetate as the acylating agent, in the presence of *Burkholderia cepacia* lipase (BCL), immobilized on diatomite. Optical purity was determined by Mosher's acid derivatization method, followed by NMR spectrum analysis. As a result, all possible enantiomers of halogenated cycloalkanols with a high degree of optical purity were obtained (Scheme 3). The absolute configuration of the obtained compounds was determined

using the Kazlauskas rule and also by chemical correlation methods, converting the reaction products into known substances from the literature and comparing their optical rotation values. In all cases, it was shown that the resolution occurred according to the Kazlauskas rule [8].



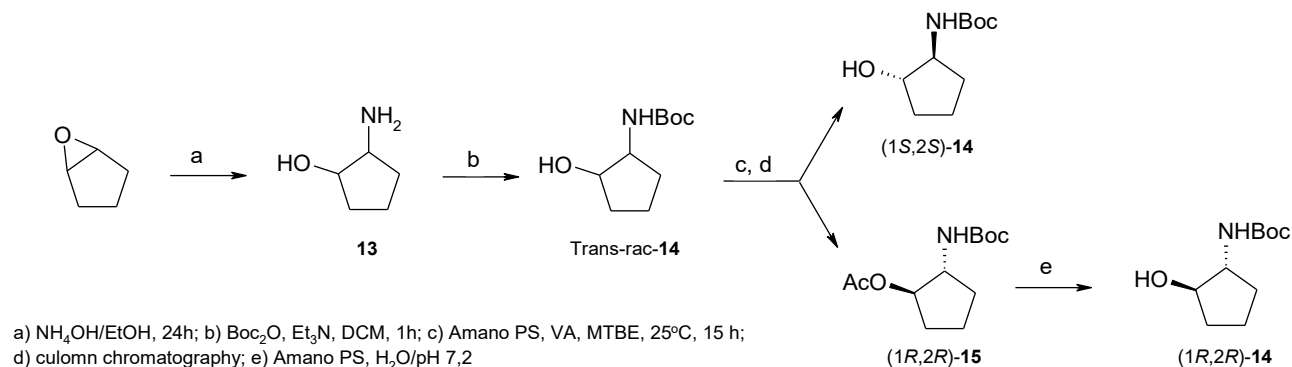
Scheme 2. Synthesis of the racemic starting compounds



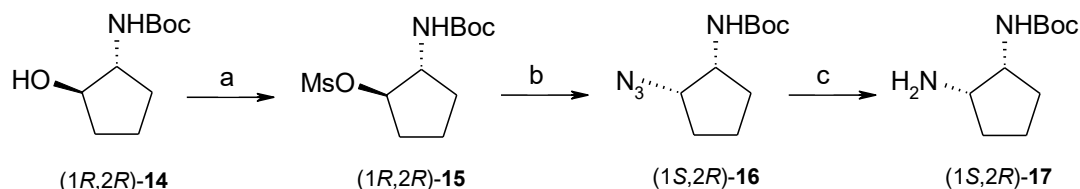
a) Amano PS, VA, MTBE, 25°C, 15 h; b) column chromatography; c) Amano PS, H₂O/pH 7,2

Scheme 3. Enzymatic resolution of cis- and trans-2-halogencycloalkanols.

Following a similar approach, a number of cyclic and aryl-cyclic compounds were synthesized. For instance, by opening the cyclopentenoxide ring and subsequently protecting the amine group with Boc anhydride, enzymatic resolution of trans-racemates 1,2-N-Boc-amino-cyclopentanol 14 was performed. Both stereoisomers were isolated in optically and chemically pure form (Scheme 4). The obtained enantiomers of trans-amino-cyclopentanol were then converted into the corresponding optically active cis-1,2-N-Boc-diamino-cyclopentanes 17 through the formation of an azide at a key stage, accompanied by the inversion of the absolute configuration of the carbon at the reaction center. Both enantiomers were isolated in optically and chemically pure form, with no racemization (Scheme 5) [9].



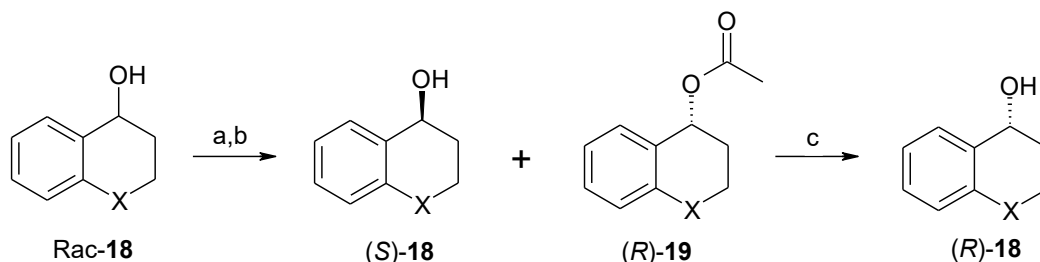
Scheme 4. Synthesis and biocatalytic resolution of trans-1,2-N-Boc-amino-cyclopentanol.



a) MsCl, Et₃N 1h; b) NaN₃, DMF 24h; c) H₂/Pd-C, 15h

Scheme 5. Synthesis of stereochemically pure cis-1,2-N-Boc-diaminocyclopentanes.

A convenient protocol for the enzymatic resolution of chroman-4-ol and its analogs (six- and seven-membered cycles with O, S, SO₂) was developed. These compounds were resolved into enantiomers from the corresponding racemic alcohols and, in most cases, were obtained with high optical purity – 91-99% *ee*. However, the resolution of certain substrates, specifically thiogomochromanols and dioxothiogomochromanols, showed lower selectivity, with the optical purity of the products being moderate – 82-85%. In such cases, a method of double enzymatic purification was applied. The obtained enantiomerically enriched stereoisomers of thiogomochromanols and dioxothiogomochromanols were subjected to a second cycle of enzymatic purification after column separation, resulting in products with a high degree of optical purity (Scheme 6). It should be noted that for the enzymatic transesterification reaction, *Burkholderia cepacia* lipase was found to be the most effective, while for the enzymatic hydrolysis of acetates, *Candida antarctica* lipase B was used [10].



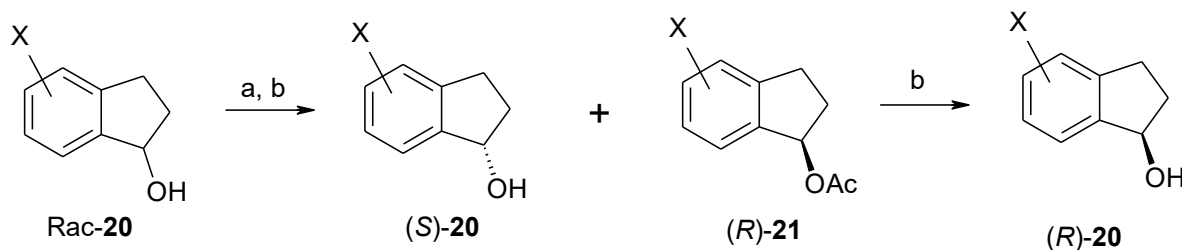
a) BCL, Isopropenyl acetate, MTBE, 25-50°C, 14-72 h; b) Column chromatography;
c) CAL-B, H₂O/pH 7,2
X=O, S, SO₂

Scheme 6. Enzymatic resolution of enantiomeric chroman-4-ol and its analogs with BCL.

Using the same protocol, the resolution of halogen-2-indanol derivatives was carried out. These compounds serve as synthetic building blocks for the development of pharmaceutical agents, insecticides, peptide nucleic acids, and bioregulators, such as Indinavir – a drug used for the treatment of human immunodeficiency virus infections, and Ladostigil – a pharmaceutical agent for the treatment of Alzheimer's disease. Consequently, all samples of fluoro-, chloro-, and bromo-dihydroindanol derivatives were resolved into (*S*)- and (*R*)-enantiomers 20, isolated, and characterized by physicochemical methods [11].

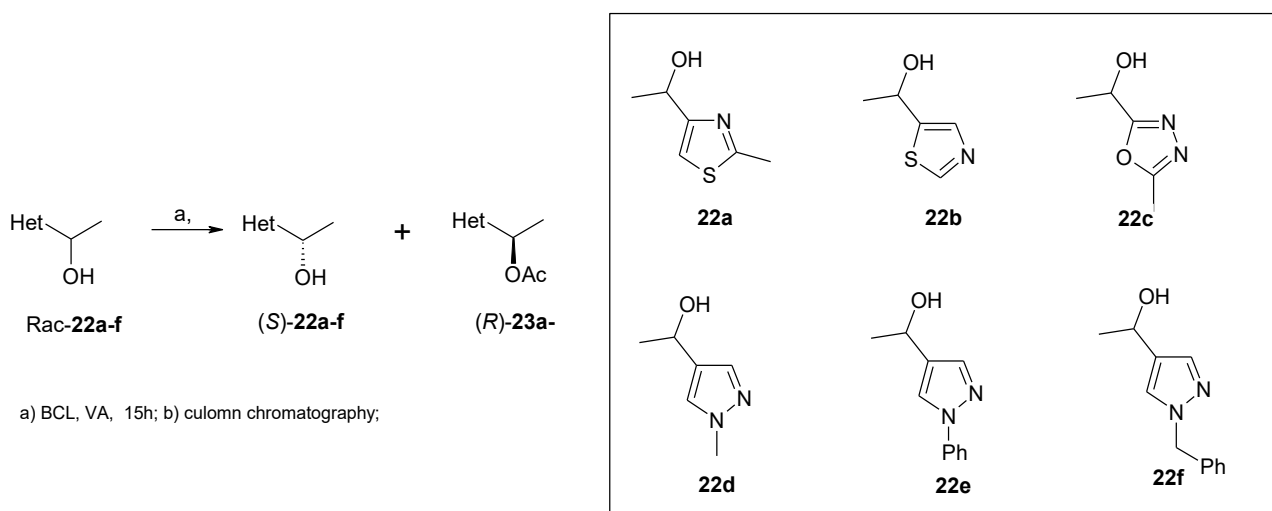
Heteroaromatic secondary alcohols are found as structural fragments in various natural compounds and pharmaceuticals. The enzymatic resolution methodology is particularly well-suited for obtaining stereochemically pure heterocyclic secondary alcohols. For instance, racemic 2-heteroaryl-ethanol derivatives, which were synthesized by reducing the corresponding ketones or through a Grignard reaction with heterocyclic aldehydes, were subjected to biocatalytic

transesterification (Scheme 8). Two immobilized lipases, BCL and CAL-B, were employed for this process. It was found that BCL was the most effective for transesterification. The hydrolysis of the obtained esters was performed using conventional alkaline hydrolysis in methanolic potassium hydroxide and enzymatic hydrolysis in the presence of lipases. The results showed that enzymatic hydrolysis yielded products with higher optical purity, with CAL-B being the most effective lipase for this reaction [12].



a) BCL, VA, 15h; b) column chromatography; c) CAL-B, Phosphate buffer pH7.2, 15h
X=F, Cl, Br

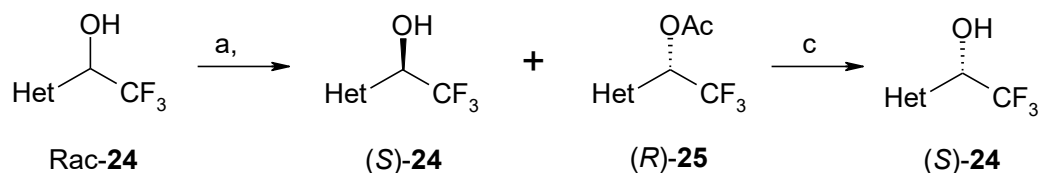
Scheme 7. Resolution of racemic halo-2,3-dihydro-1H-indenols Rac-20 via enzymatic esterification



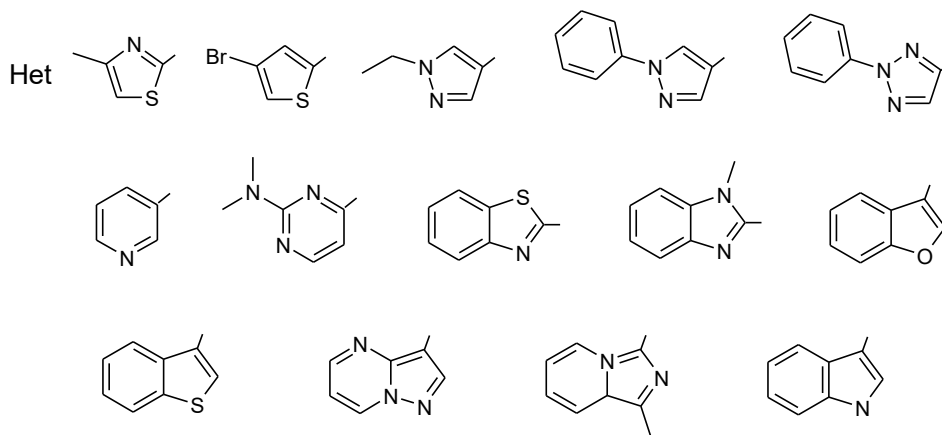
a) BCL, VA, 15h; b) column chromatography;

Scheme 8. Lipase-catalyzed acetylation of racemic 1-heteroarylethanol.

1-Substituted 2,2,2-trifluoroethanols attract attention due to their potential use as building blocks for incorporating chiral CF₃ fragments into biologically active compounds, as promising functional materials, and as carboxyl group mimetics. Therefore, we focused our efforts on developing methods for obtaining these compounds in optically pure form. Racemic alcohols were synthesized by reducing the corresponding ketones using NaBH₄ or from the respective aldehyde and Rupert-Prakash reagent. The resolution was carried out following the protocol described above (Scheme 9). As with 2-heteroarylethanol, for 2,2,2-trifluoro-1-(heteroaryl)ethanol, the best lipase for enzymatic transesterification was BCL, and for hydrolysis, it was CAL-B. It should be noted that in the case of 2,2,2-trifluoro-1-(heteroaryl)ethanol, the reaction conditions were harsher compared to 1-heteroarylethanol: the separation reaction temperature was 45-50°C, and the reaction time reached up to 96 hours. This can be attributed to the steric effects caused by the CF₃ group and the electronegativity of the CF₃ group [13].

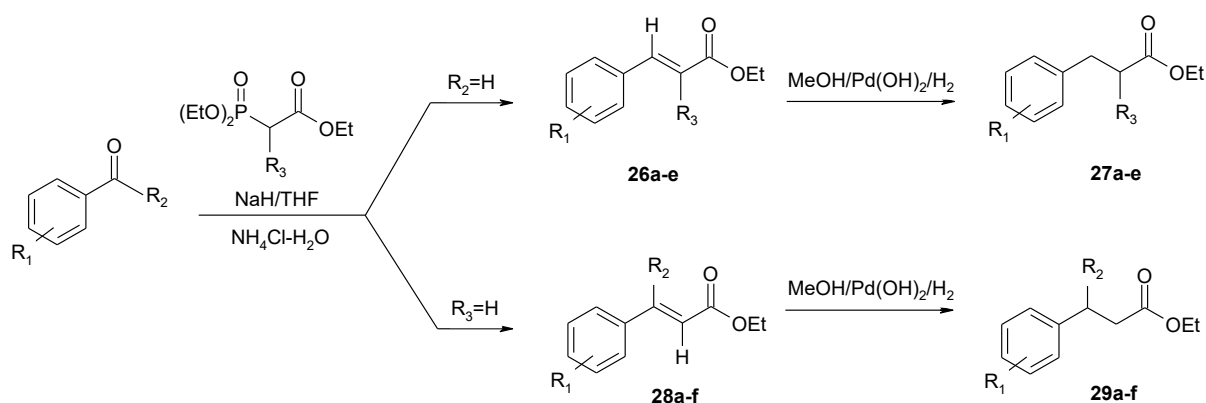


a) BCL, Isopropenyl acetate, MTBE, 35-45 °C, 15-96 h; b) Column chromatography;
 c) BCL, H₂O/pH 7,2



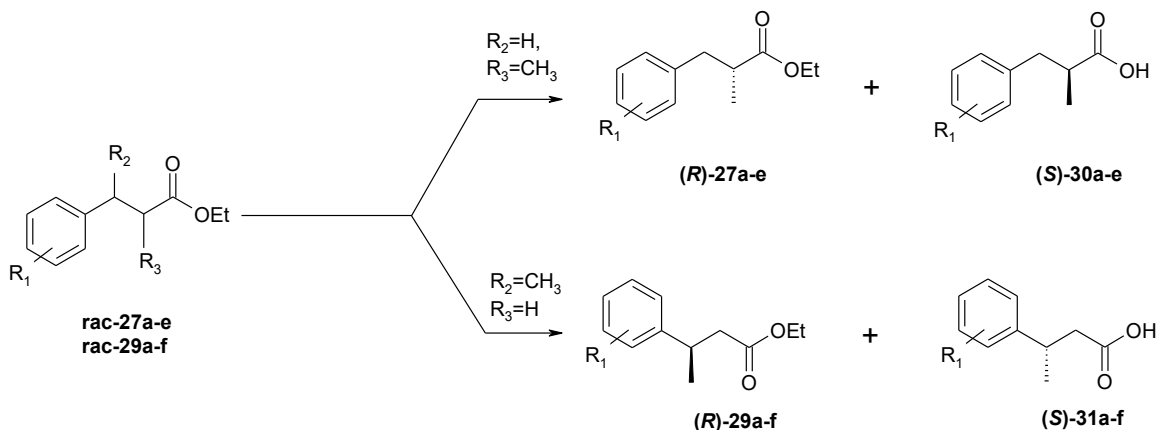
Scheme 9. Enzymatic resolution of 2,2,2-trifluoro-1-(heteroaryl)ethanols.

Enantiomerically pure 3-arylalkanoic acids are used as chiral synth in the asymmetric synthesis of antibacterial agents, biologically important substances, as well as in amino acid synthesis. We carried out the deracemization of 3-aryl-2-methylpropanoates and ethyl 3-arylbutanoates in the presence of BCL. Racemic arylcarboxylic acids were obtained according to a two-step procedure, through the Horner-Wittig reaction of the corresponding carbonyl compounds followed by hydrogenation in methanol in the presence of a palladium catalyst (Scheme 10).



Scheme 10. Synthesis of racemic ethyl 3-aryl-2-methylpropanoates **27a-e** and ethyl 3-arylbutanoates **29a-f**.

The enzymatic hydrolysis of racemic esters of arylcarboxylic acids was carried out in a phosphate buffer at pH 7.0 using Amano PS lipase. As a result, arylcarboxylic acids **30a-e** or **31a-f** were obtained with yields of 52-60% and enantiomeric purity ranging from 77% to 99% (Scheme 11). To increase the enantiomeric purity of the arylcarboxylic acids, a double enzymatic deracemization was performed [14].



Scheme 11. Enzymatic resolution of enantiomeric racemic arylcarboxylic acids esters **27a–e** and **29a–f**.

Conclusion

The enzymatic resolution has proven to be a highly efficient and selective method for obtaining enantiomerically pure compounds, which are important for the pharmaceutical and agrochemical industries. Mild reaction conditions, such as moderate temperature and neutral pH, minimize side reactions and ensure the preservation of sensitive substrates. Furthermore, the environmental safety of biocatalysis, which often eliminates the need for harsh reagents or metallic catalysts, makes it a sustainable alternative to traditional separation methods. The wide range of substrates applicable to the enzymatic process, including alcohols, amines, and carboxylic acids, highlights its versatility in asymmetric synthesis. With high enantioselectivity ($ee > 99\%$) and scalability, enzymatic resolution remains a valuable tool both in laboratory research and industrial production.

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Preparation of Enantiomerically Pure 3-Heteryl-2-Methylpropanoic and 3-Heterylbutanoic Acids by Enzymatic Kinetic Resolution

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Abstract. *A new approach has been developed for synthesizing important compounds with potential biological activity – enantiomerically pure 3-heteryl-2-methylpropanoic and 3-heterylbutanoic acids. The kinetic dynamic enzymatic resolution methodology was applied at key synthesis stages. A dual biocatalytic purification method was employed to achieve a high degree of optical purity of the obtained products. The resulting amines are promising building blocks for the development and production of new pharmaceuticals and biologically active compounds.*

Keywords: biocatalysis; chiral heterocyclic compounds; chiral 3-heterylbutanoic acids; 3-heteryl-2-methylpropanoic acids; lipase; enzymatic resolution, optical activity.

Introduction

Heterocyclic compounds play an extremely important role in pharmacology, as they form the basis of many pharmaceutical drugs. Approximately 75–90% of registered pharmaceutical compounds contain heterocyclic structures. [1] This is due to a range of properties and characteristics of these compounds, such as a broad spectrum of biological activity, pharmacophoric nature, structural diversity, the ability to enhance drug solubility, penetration through biological membranes, and stability within the body. [2,3] Heterocyclic aliphatic carboxylic acids represent an intriguing class of nitrogen-containing organic compounds that exhibit diverse biological and pharmacological activities. Among them are important pharmaceutical agents such as antibiotics, non-steroidal anti-inflammatory drugs, antiviral agents, histamine antagonists, and GABA inhibitors. [4-7] They are also widely used as precursors in the synthesis of many biologically significant compounds. [8]

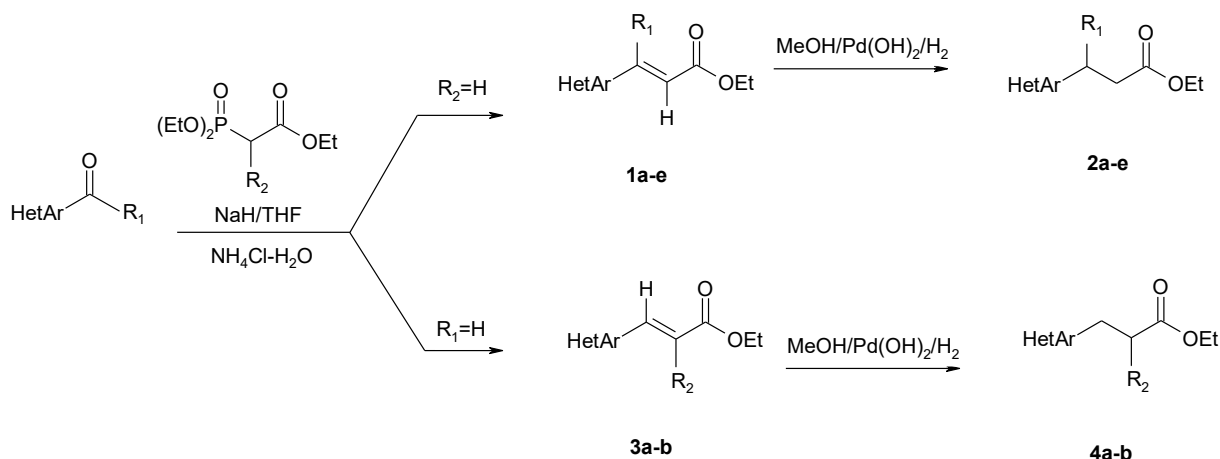
In recent years, there has been a significant increase in the use of chiral pharmaceutical agents. The regulatory requirements on this matter were published by the U.S. Food and Drug Administration (FDA) as early as 1992 in a document titled *Development of New Stereoisomeric Drugs* [9, 10]. In accordance with these requirements, there has been a substantial shift toward the development of enantiomerically pure pharmaceuticals. As a result, the demand for enantiomerically pure drugs is growing annually by 13–15% [11, 12]. Therefore, the development of new, simple, accessible, cost-effective, and environmentally friendly methods for obtaining such compounds remains a highly relevant task in modern chemistry.

Chiral, enantiomerically pure 3-heteryl-2-methylpropanoic acids, and 3-heterylbutanoic acids are scarcely described in the literature. In their racemic form, they have been synthesized via the Horner–Wittig reaction, starting from the corresponding heterylcabonyl compounds [13]. In a stereochemically pure form, they have been obtained through asymmetric hydrogenation using chiral cobalt-based catalysts, though the optical yields in this case remained moderate [14].

Therefore, in our work, we have developed a method for obtaining stereochemically pure 3-heteryl-2-methylpropanoic and 3-heterylbutanoic acids through enzymatic kinetic resolution using lipases as biocatalysts.

Results and discussion

At the first stage of our work, racemic esters of 3-heteryl-2-methylpropanoic and 3-heterylbutanoic acids (**2a–e** and **4a–b**) were synthesized. To obtain them, we employed the approach previously described by us [15], following the two-step procedure shown in Scheme 1 below.



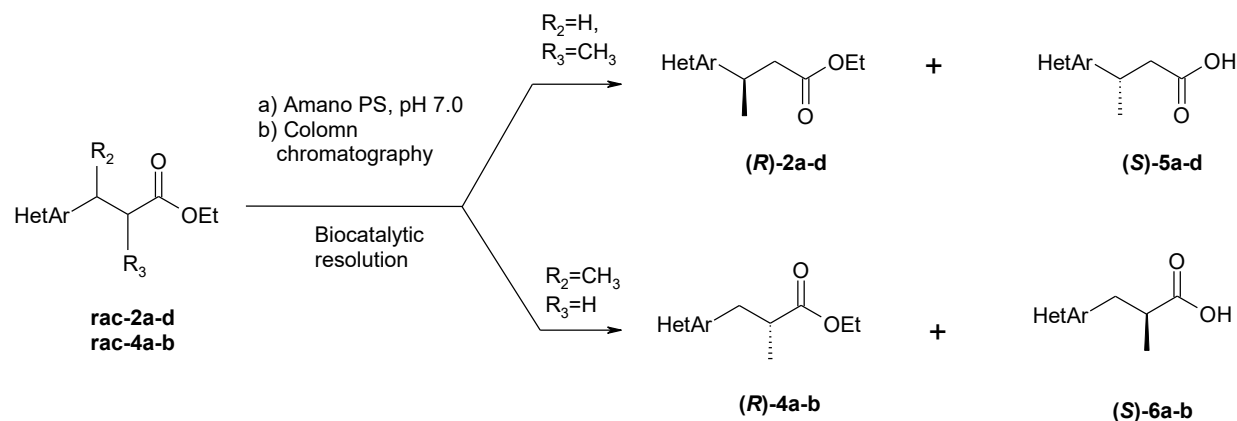
Compound	HetAr	R ₁	R ₂
2a	2-Pyridine	H	CH ₃
2b	3-Pyridine	H	CH ₃
2c	4-Pyridine	H	CH ₃
2d	5-Pyrazole	H	CH ₃
4a	3-Pyridine	CH ₃	H
4b	4-Pyridine	CH ₃	H

Scheme 1. Synthesis of racemic esters of 3-heterylbutanoic acids and 3-heteryl-2-methylpropanoic acids.

Thus, by applying the Horner–Wittig reaction at a key stage, unsaturated heterylcарboxylic acids **1a–d** and **3a–b** were obtained from the corresponding substituted heterocyclic carbonyl compounds and ethyl 2-(diethoxyphosphoryl)acetate. These intermediates were then hydrogenated in the presence of palladium hydroxide. As a result, racemic 3-heterylbutanoic acids **2a–e** and 3-heteryl-2-methylpropanoic acids **4a–b** were obtained in ~90% yields and were used in further transformations without additional purification.

The next stage involved obtaining enantiomerically pure isomers of heterylcарboxylic acids. To achieve this, enzymatic kinetic resolution was employed using lipases as biocatalysts. A selection of highly efficient and highly selective enzymes was tested, including lipases from *Burkholderia cepacia* (Amano PS), *Pseudomonas cepacia*, and *Candida antarctica* B. Among these, Amano PS lipase proved to be the most effective in hydrolyzing racemic esters of heterylcарboxylic acids.

The enzymatic hydrolysis was carried out in an aqueous medium using a phosphate buffer at pH 7.0 with Amano PS lipase [15–17]. As a result, all enantiomers of 3-heterylbutanoic acids (**2a–d**) and 3-heteryl-2-methylpropanoic acids – (*R*)-esters **2a–d**, **4a–b** and (*S*)-acids **5a–d**, **6a–b** – were obtained with yields of 52–60% and enantiomeric purity of 97–100% (Scheme 2).



Compound	(R)-Ester			Compound	(S)-Acid		E_a
	HetAr	Yield, %	ee, %		Yield, %	ee, %	
2a	2-Pyridine	40	97	5a	38		>100
2b	3-Pyridine	41	100	5b	40	100	>100
2c	4-Pyridine	38	97.5	5c	45	100	>100
2d	5-Pyrazole	35	100	5d	37	100	>100
4a	3-Pyridine	39	100	6a	42	100	>100
4b	4-Pyridine	40	99	6b	40	97.5	>100

Scheme 2. Biocatalytic enantioselective resolution of heterylcarboxylic acid esters.

Next, the obtained (*R*)-esters 2a–d, 4a–b were subjected to acidic hydrolysis by boiling in 3N hydrochloric acid, yielding good, quantitative results without the need for additional purification (Scheme 3). In all cases, the hydrolysis proceeded without racemization, preserving the absolute configuration of the compounds. As a result, all stereoisomers of 3-heterylbutanoic acids **5a–d** and 3-heteryl-2-methylpropanoic acids **6a–b** were obtained. They were characterized using available physicochemical methods (Table 1).

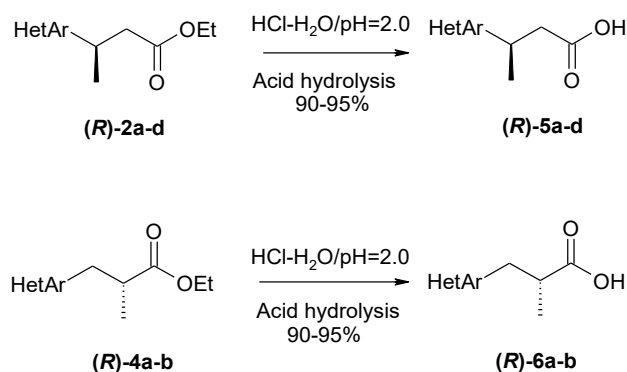
Scheme 3. Acid hydrolysis of (*R*)-heterylcarboxylic acid esters.

Table 1

3-Phenylbutanoic acids and methyl-3-phenylpropanoic acids							
№	Compound	Optical Rotatory Power			HPLC		
		ee, %	$[\alpha]_D^{20}$	C (g/100 mL); solvent	τ (R) (min.)	τ (S) (min.)	Conditions
1	(R)-5a	97	−14.86	0.5, MeOH	12.362	9.606	a
2	(S)-5a	97.5	+15.36	0.5, MeOH	12.081	9.656	a
3	(R)-5b	100	−30.91	0.5, MeOH	12.682	-	b
4	(S)-5b	100	+32.36	0.5, MeOH	-	17.407	b
5	(R)-5c	97.5	−26.95	0.5, MeOH	7.465	6.278	c
6	(S)-5c	100	+29.97	0.5, MeOH	-	6.852	c
7	(R)-5d	100	−3.17	0.5, MeOH	17.947	-	d
8	(S)-5d	100	+2.22	0.5, MeOH	-	16.531	d

13	(S)-6a	100	-38.71	0.5, CH ₂ Cl ₂	47.881	-	e
14	(R)-6a	100	+38.18	0.5, CH ₂ Cl ₂		41.411	e
15	(S)-6b	97.5	-28.26	0.5, CHCl ₃	4.071	3.615	f
16	(R)-6b	99	+28.46	0.5, CHCl ₃	-	3.442	f

Conditions: **a** Column: Chiralpak AD-H (250 × 4.6 mm, 5 mkm) – 3; Mobile Phase: Hexane: IPA:MeOH, 50:25:25; Flow Rate, 0.6 mL/min. **b** Column: Chiralcel OJ-H (250 × 4.6 mm, 5 mkm) – 3; Mobile Phase: Hexane(0.1%TFA):IPA:MeOH, 70:15:15; Flow Rate, 0,6 mL/min. **c** Column: Chiralpak AD-H (250 × 4.6 mm, 5 mkm – 3; Mobile Phase: CO₂:MeOH, 90:10; Flow Rate, 2.0 mL/min. **d** Column: Chiralpak AD-H (250 × 4.6 mm, 5 mkm) – Mobile Phase: Hexane (0.1% TFA): IPA, 90:10; Flow Rate, 0.6 mL/min. **e** Column: Chiralcel OJ-H (250 × 4.6 mm, 5 mkm) – OJH0CE–UF008 – 3; Mobile Phase: Hexane(0.1%TFA):IPA(0.1%TFA):MeOH(0.1%TFA), 90:5:5; Flow Rate, 0.6 mL/min. **f** Column: Chiralpak AD-H (250 × 4.6 mm, 5 mkm) – 3; Mobile Phase: CO₂:MeOH, 80:20 ; Flow Rate, 2.0 mL/min

Conclusion

In this work, we obtained and described all optical isomers of 3-heterylbutanoic and 3-heteryl-2-methylpropanoic acids. For this purpose, a method of biocatalytic kinetic resolution of racemates of the esters of these acids was employed. Different lipases were used as biocatalysts, namely *Burkholderia cepacia* Amano PS lipase, *Pseudomonas cepacia* lipase, and *Candida antarctica* B lipase. The most effective lipase for the enzymatic hydrolysis of the esters of these acids was found to be Amano PS lipase. All optically active heterylcboxylic acids were obtained with high chemical yields, optical purity >95%, and the preservation of the absolute configuration of the chiral center. These compounds were described and characterized using modern physicochemical methods.

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The Content of Anthocyanins and Ascorbic Acid in Extract of *Malva Sylvestris* L. Obtained by Enzyme-Assisted Extraction

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Abstract. *Modern science provides various methods for the extraction of phytochemicals: conventional and unconventional. The unconventional technique incorporates some features to optimize traditional methods. The aim of this study was to investigate a new environmentally friendly method to enhance realizing of bioactive compounds from Malva sylvestris L. - enzyme-assisted extraction.*

Keywords: *Malva sylvestris* L., enzyme-assisted extraction, phytochemicals, anthocyanins, ascorbic acid.

Introduction

Malva sylvestris L., or mallow, as a colored-flowering plant, contains anthocyanins [1] and ascorbic acid. Extraction of these bioactive compounds from the *Malva* genus is typically accomplished by maceration using different organic solvents [2, 3]. Compared to that, new methods offer a technique named “new-generation solvents”, which are water buffers. Enzyme-assisted extraction (EAE) is a “green chemistry” technique used in this study. The EAE process includes the ability of the enzyme to hydrolyze plant cell walls and facilitate the bioactive compounds [4].

Anthocyanins are phenolic compounds and flavonoids, which mostly form the colour of flowers (red, blue, purple). Due to their fair stability, some anthocyanins, such as malvidin and petunidin, which were studied in this work, are glycosylated and acylated [5]. The extraction of anthocyanins needs to be carried out at low temperatures, even though they have low stability to heat. Conventional method applications are limited due to the long duration of the process, but with low facilitation of bioactive compounds [6]. Compared to this enzyme-assisted extraction, an unconventional method, releases anthocyanins from the vacuoles. Also, an acidic condition used in this technique is common for a more stable flavinium form [5, 7]. Mallows' anthocyanins have proven therapeutic applications, including antiradical [8], antimicrobial [9], reducing the level of cholesterol [1], etc.

Ascorbic acid or vitamin C is water-soluble in water ketolactone with a carbon ring consisting of 5 atoms. This molecule has strong free radical scavenging ability, which is linked to C2 and C3 carbons [10]. Similarly, classic methods consume solvents that are mostly organic and hazardous to the environment. Enzyme-assisted extraction is performed under mild conditions with a water-based solvent that doesn't affect vitamin C [11].

Materials and methods

Malva sylvestris L. plant material (leaves and flowers) from the natural growing area was dried in the shade and then ground to 4 mesh.

Enzyme-assisted extraction: 2 g of *M. sylvestris* plant material was soaked for 30 min in 100 ml of acetic buffer (pH 4), then the mixture was placed in a water bath at 56.90 °C, and after 20 min, enzyme cellulase was added (producer “ENZYM”, Ukraine) to the preheated solvent with

plant material. The duration of extraction was 57.40 min. The extract was filtered and stored in a dark place [12].

Anthocyanins content (pH differential method): 200 µl of extract was diluted with 0.8 ml of two different buffers, 0.025 M potassium chloride buffer (pH 1.0) or 0.4 M sodium acetate buffer (pH 4.5). After 15 minutes of incubation, samples were measured at a spectrophotometer, Specord M40, with different wavelengths for each of the studied anthocyanins (Table 1) [13].

Table 1

Values for anthocyanins measurement

Anthocyanins	Wavelength, nm	Molar absorptivity, ε	Molecular weight
Pelargonidin	505	15.600	271.24
Peonidin	511	37.200	301.27
Cyanidin	510	24.600	287.24
Malvidin-3-glucoside	519	28.000	493.4
Delphinidin	523	34.700	303.24

The calculations were carried out using formulas (1) and (2), where l – length of the cuvette (1.00), DF – dilution factor, and 700 nm was used as a standard. The results were expressed as micrograms of anthocyanins in grams of dried plant weight (µg/g DW).

$$A = (A_x - A_{700})pH_{1.0} - (A_x - A_{700})pH_{4.5} \quad (1)$$

$$A_{ant} = \frac{A * MW * DF * V}{\epsilon * l * m} \quad (2)$$

Ascorbic acid content: ascorbic acid solution was used as a standard: 100 to 40 µl was mixed with 500 µl of 10% Folin-Ciocalteu reagent solution in water and then was adjusted with 900 µl of 10 % water solution of trichloroacetic acid and held for 10 min. The primary sign of the reaction is the reduction of the blue colour. The same procedure was used for extract samples. Spectrophotometry was performed at 706 nm by using a Specord M40 spectrometer. Ascorbic acid was expressed as µg of ascorbic acid per g of dried weight (DW) [14].

Results and discussion

The results of the anthocyanins assay are shown in Table 2, while the chemical formulas are presented in Fig. 1. Malvidine-3-glucoside emerged as the predominant anthocyanin, exhibiting the highest concentration within the extract. In contrast, pelargonidin has a smaller amount, while peonidin is the least abundant. Bahambari, N. et. al also revealed that malvidin has higher content in *Malva sylvestris* [15].

Table 2

Content of anthocyanins in the enzymatic extract of *Malva sylvestris*

Anthocyanins (mg QE/g DW)	
Pelargonidin	0.0367
Peonidin	0.0200
Cyanidin	0.0283
Malvidin-3-glucoside	0.0501
Delphinidin	0.0247

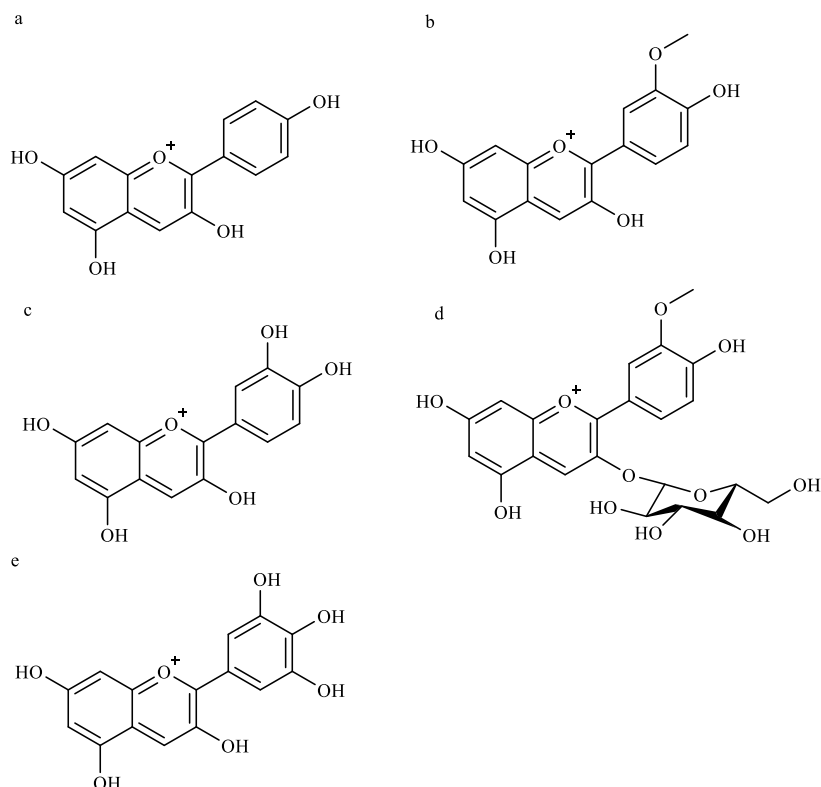


Fig. 1 Anthocyanins of *Malva sylvestris*: a - pelargonidin; b - peonidin; c - cyanidin; d - malvidin-3-glucoside; e – delphinidin.

To perform further calculations, a calibration curve for ascorbic acid was established. The curve included a concentration range from 10 to 25 $\mu\text{g}/\text{ml}$. The resulting data were illustrated in Fig. 2.

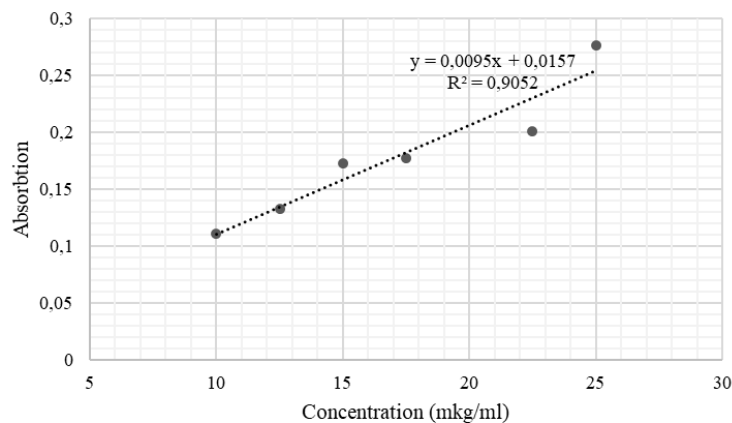


Fig. 2 Calibration curve of ascorbic acid.

The extract revealed a concentration of ascorbic acid measured as 53.4248 $\mu\text{g}/\text{g}$ DW. These findings highlight the statement that mallow is a potential source of this compound [16].

Conclusions

Enzyme-assisted extraction of *Malva sylvestris* L. anthocyanins and ascorbic acid demonstrated a high yield of these compounds. The promising outcome leads to continued studying of this extraction method, which enhances the yield for other bioactive compounds.

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GREEN CHEMISTRY

Design and Research of Eco-Friendly Biodegradable Composites Based on Renewable Biopolymer Materials and Reed Waste

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Abstract. *Nowadays, an active transition from limited, carbon-intensive resources to renewable, carbon-neutral sources is at the heart of the bioplastics revolution. Therefore, the development of effective bioplastics represents a paradigm shift in materials science, the goal of which is to combine the functionality of traditional plastics with environmentally safe properties. Environmentally safe composites based on a renewable bioplastic blend of pea starch with the addition of reed waste as a filler. The physico-chemical features of the structure and surface, as well as the technological characteristics of reed waste, as the organic fillers for a renewable bioplastic blend of pea starch, were studied. The effect of the fractional composition analysis, morphology, and nature of reed waste on the quality of the design, environmentally safe, biodegradable composites, and their ability to disperse in the matrix of a renewable bioplastic blend of pea starch was carried out. The influence of different content and morphology of reed waste on the set of technological and operational characteristics of the developed environmentally safe biodegradable composites was investigated. Optimization studies were conducted to determine the most effective composition of the environmentally safe biodegradable composites. It is shown that the most optimal direction for obtaining strong, environmentally safe, biodegradable composites based on a renewable bioplastic blend of pea starch is associated with the use of waste reed stalks, with its optimal content at the level of 60 wt. %.*

Keywords: environmental safety, biodegradable, composites, renewable biopolymers, organic waste, reed, hemp.

Introduction

Nowadays, the world is faced with a global problem of accumulation of polymer waste, which leads to environmental pollution, depletion of natural resources, and negative impact on ecosystems [1]. Because of this, the development of new biodegradable polymers as a potential solution to these problems is gaining special attention and relevance. Today, the development of this scientific and technical direction is important to reduce the man-made burden on the planet and preserve natural resources [2].

One of the main directions of development of biodegradable polymers is their ability to degrade under the influence of environmental factors, thereby reducing the problem of accumulation of polymer waste. But the relevance of their use is also increasing in conditions of limited fossil raw materials, which are the basis for the production of many traditional polymers. The transition to biodegradable materials, which are mostly obtained from renewable sources, such

as starch, cellulose, chitin, and other biopolymers, is considered an important step towards a circular economy and reducing the carbon footprint [3].

Literature reviews often emphasize the diversity of biodegradable polymers and their properties. Researchers are actively studying and modifying existing biopolymers, as well as developing new composite materials based on them to expand their scope of application. Particular attention is paid to improving mechanical properties, thermal stability, barrier properties, and other key parameters, which will allow biodegradable polymers to successfully compete with traditional plastics in various industries, including packaging, agriculture, medicine, and textiles [4].

At the same time, literature sources also highlight the existing challenges and limitations associated with the mass introduction of biodegradable polymers [5,6]. These include, in particular, the higher cost of production compared to traditional plastics, the need to create an appropriate infrastructure for their disposal (composting), as well as the potential impact on land use and food security in the case of large-scale use of agricultural crops as raw materials [7]. But despite all the challenges, the relevance of research in the field of biodegradable polymers remains high. Scientists continue to work on improving their production technologies, reducing costs, improving performance characteristics, and developing effective methods for their recycling and disposal [3]. Governments of many countries are also implementing legislative initiatives aimed at stimulating the use of biodegradable materials and limiting the use of traditional single-use plastics [4]. The development of the environmentally safe biodegradable polymer industry helps to solve modern environmental and economic challenges. Biodegradable polymers are considered a key element of strategies to reduce polymer waste and preserve natural resources for future generations.

Combining biopolymers with plant fillers allows obtaining environmentally safe composite materials with completely new technological and operational properties [7,8]. Although traditionally special attention is paid to the effect of plant fillers on mechanical strength, which has led to their widespread distribution into reinforcing or reinforcing and non-reinforcing or inert, fillers are capable of having many other effects, which determine the high efficiency of their use: reduction of fluidity and volumetric thermal or chemical shrinkage, improvement of moldability and dimensional stability, reduction of flammability, increase of frictional or antifrictional, electrical, thermal-physical and other characteristics [9,10]. In rare cases, plant fillers play the role of only volume fillers, which are introduced to reduce the cost of environmentally safe composite materials or reduce the volume of the biopolymer used [11,12]. Plant fillers for the production of environmentally safety composite materials can be practically all materials existing in nature and created by man, including the polymers themselves, after giving them a certain shape or size - in the form of spheres, powders, with irregularly shaped particles, flakes, ribbons, fibers, etc., distributed in different ways and in different ratios in the polymer matrix [13,14].

Analysis of literature sources [15,16] showed that the main components of environmentally safe composite materials based on plant waste are a biodegradable polymer matrix, an organic filler, and various functional additives, such as antiseptics, flame retardants, compatibilizers, etc.

The purpose of the research is to design and research environmentally safe biodegradable composites based on renewable biopolymer materials and reed waste.

Methodology

The following materials are investigated in the article:

- thermoplastic composites based on pea starch with the addition of various types of additives;

- waste of marsh reed stems, which were collected in the Kharkiv region and crushed in a Braun blender to a size of 0.5-6 mm - Fig. 1;

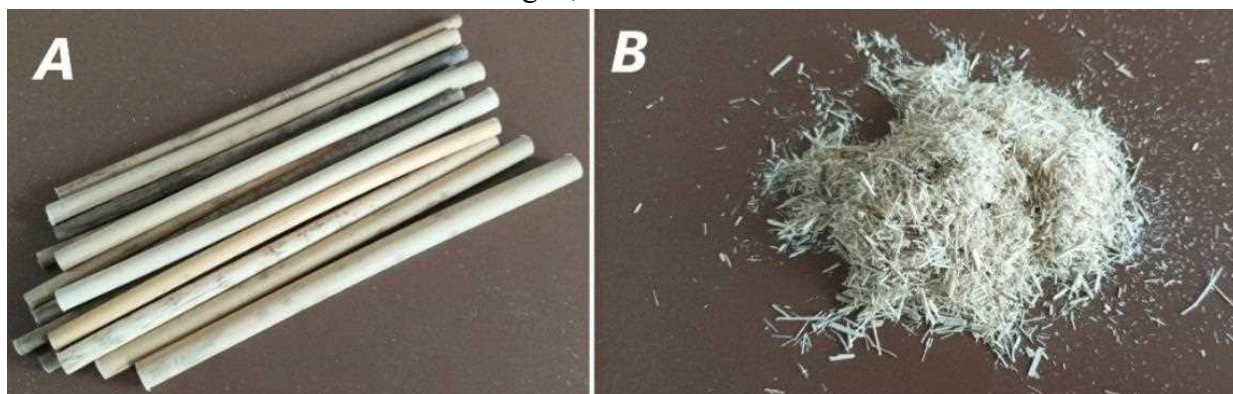


Fig. 1. Photos: A – reed stem waste, B – crushed reed stem waste.

Samples of environmentally safe biodegradable composites based on renewable biopolymer materials and reed waste were obtained on a laboratory extruder with varying formulation composition and temperature regimes. At the first stage of the study, mixtures with different quantitative ratios of the following components were prepared: pea starch, solvent, plasticizer, initiator, and crosslinking agent. At the second stage, the temperature regime for processing the mixtures was selected by an experimental method.

In the process of determining the optimal processing regime, it was found that each of the formulations has its own processing temperatures. At the third stage, experimental samples of thermoplastic composites based on pea starch were obtained (Fig. 2). In formulation ST1, the solvent prevailed, in formulation ST2, the plasticizer prevailed, and in formulation ST3, the crosslinking catalyst prevailed.

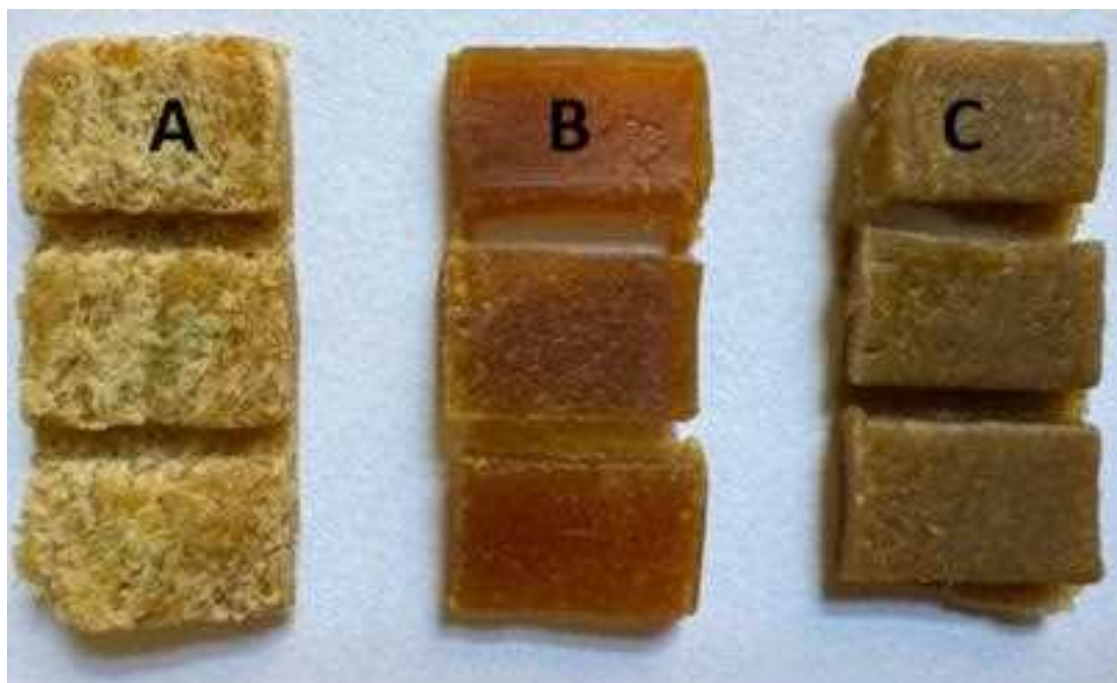


Fig. 2. Environmentally safe biodegradable thermoplastic composites based on pea starch composites: A- ST1; B - ST2; C - ST3.

After conditioning the samples (72 hours), the melting temperatures of the environmentally safe biodegradable thermoplastic composites based on pea for each recipe were investigated to more clearly determine the phase transitions.

Thermal stability of environmentally safety biodegradable thermoplastic composites based on pea starch and composites based on renewable biopolymer thermoplastic pea starch and reed waste in terms of melting and destruction temperature ranges was determined according to ISO 3146 on a laboratory brass disk with a diameter of 50 mm and a thickness of 19 mm with a side hole for a thermometer with a diameter of 9 mm.

The study of impact strength and breaking stress during bending of the environmentally safety biodegradable thermoplastic composites based on pea starch and composites based on renewable biopolymer thermoplastic pea starch and reed waste without notching at a temperature of 20 °C was carried out on a pendulum head according to ISO 180 and ISO 178, respectively, on samples conditioned under standard controlled temperature and humidity for those standards.

Microscope studying was done using an electronic microscope, Digital Microscope HD color CMOS Sensor (China).

Results and discussions

Fig. 3 shows environmentally safe biodegradable thermoplastic composites based on pea starch, sequential increase in temperature °C:

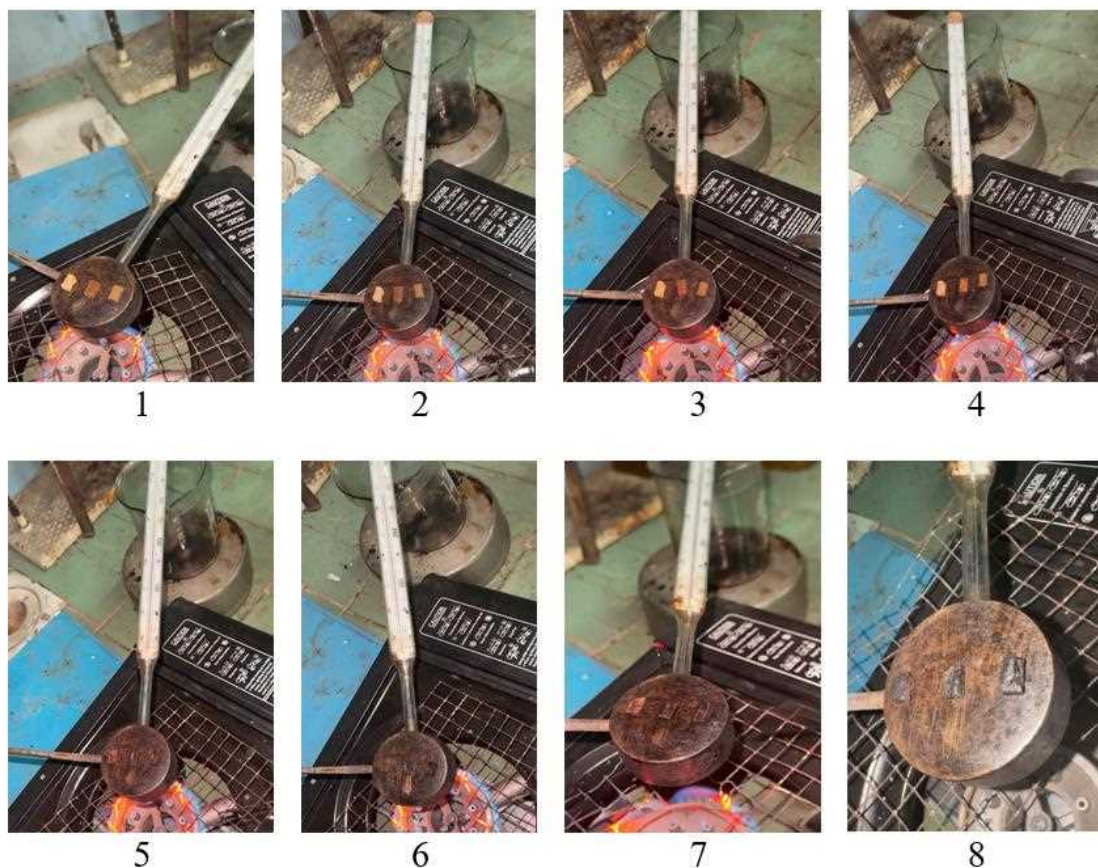


Fig.3. Study of the melting point of environmentally safety biodegradable thermoplastic composites based on pea starch: 1) 40 °C; 2) 100 °C; 3) 150°C; 4) 180 °C; 5) 250 °C; 6) 280 °C; 7) 300 °C; 8) 320 °C.

At stages 1, 2 – no changes in the composites were observed. At stages 3, 4 – slight softening of the samples was observed and a characteristic odor appeared, indicating thermal destruction. At stages 5-7 – darkening of the color of the samples and their partial charring were observed. At stage 8, the composite samples completely changed color to black, indicating thermal destruction and their complete charring. During the study, it was determined that none of the samples under the influence of temperature entered a viscous state. This may indicate that during the conditioning

period, internal crosslinking occurred in the structure of the composites, which affected their thermoplastic properties.

The strength indicators of the developed environmentally safe biodegradable thermoplastic composites based on pea starch are given in Table 1.

Table 1

Strength indicators of thermoplastic composites based on pea starch

Environmentally safe biodegradable thermoplastic composites based on pea starch	Strength indicators of composites based on pea starch	
ST1	Impact strength, kJ /m ²	5.55
	Static bending strength, MPa	-
ST2	Impact strength, kJ /m ²	14.29
	Static bending strength, MPa	-
ST3	Impact strength, kJ /m ²	16.67
	Static bending strength, MPa	-

From the obtained data, it is clear that the environmentally safe biodegradable thermoplastic composites based on pea starch made according to different formulations have different strength indicators. It should be noted that the strength indicator during static bending for all three environmentally safe biodegradable thermoplastic composites based on pea starch, developed according to formulations ST1, ST2, and ST3, could not be determined due to the high elasticity of the material. Analyzing the obtained results of environmentally safety biodegradable thermoplastic composites based on pea starch strength indicators, we can conclude that the composites obtained according to the ST1 recipe have the lowest impact strength at the level of 5.5 kJ/m², in contrast to the composites obtained according to the ST2 and ST3 recipes, which have indicators of 14.29 kJ/m² and 16.67 kJ/m², respectively.

At the next stage of research, it was interesting to develop and investigate environmentally safe biodegradable composites based on renewable biopolymer materials and reed waste, based on the ST2 formulation with organic dispersed filler, crushed reed. At this stage of research, we focused on the ST2 formulation. The choice of this formulation was due to the fact that at the homogenization stage, it had a stable and homogeneous melt; therefore, the ST2 composition was determined as more technological.

Table 2 shows the strength indicators of environmentally safe biodegradable composites based on renewable biopolymer materials and reed waste. Analyzing previous studies [our article is a kind of physico-mechanical article on filling with buckwheat and oats], at the initial stage, the following filling ranges were selected: environmentally safe, biodegradable thermoplastic composites based on pea starch 60 % wt. - organic dispersed filler 40 % wt. and environmentally safe biodegradable thermoplastic composites based on pea starch 40 %wt. - organic dispersed filler 60 % wt.

From the obtained data of strength indicators studies, it is clear that filling of environmentally safe biodegradable thermoplastic composites based on pea starch ST2 with organic dispersed fillers in the form of crushed reed has a positive effect on the strength characteristics. In particular, the filling has a positive effect on the strength index during static bending of composites, giving them rigidity. With a sufficiently high filling, the impact strength remains at a high level. It is shown that the most optimal direction for obtaining strong, environmentally safe biodegradable composites based on the renewable bioplastic blend of pea

Table 2

Strength indicators of environmentally safe biodegradable thermoplastic composites based on pea starch ST2 with organic dispersed fillers in the form of crushed reed

Environmentally safe biodegradable thermoplastic composites based on pea starch	Strength indicators of composites based on pea starch	
environmentally safe biodegradable thermoplastic composites based on pea starch 60 % wt. - organic dispersed filler 40 % wt	Impact strength, kJ /m ²	15.37
	Static bending strength, MPa	90.8
environmentally safe biodegradable thermoplastic composites based on pea starch 40 %wt. - organic dispersed filler 60 % wt.	Impact strength, kJ /m ²	8.43
	Static bending strength, MPa	93.8

starch is associated with the use of waste reed stalks, with its optimal content at the level of 60 wt. %.

Conclusions

Environmentally safe composites based on a renewable bioplastic blend of pea starch with the addition of reed waste as a filler. The physico-chemical features of the structure and surface, as well as the technological characteristics of reed waste, as the organic fillers for a renewable bioplastic blend of pea starch, were studied. The effect of the fractional composition analysis, morphology, and nature of reed waste on the quality of the design, environmentally safe, biodegradable composites, and their ability to disperse in the matrix of a renewable bioplastic blend of pea starch was carried out. The influence of different content and morphology of reed waste on the set of technological and operational characteristics of the developed environmentally safe biodegradable composites was investigated. It is shown that the most optimal direction for obtaining strong, environmentally safe, biodegradable composites based on a renewable bioplastic blend of pea starch is associated with the use of waste reed stalks, with its optimal content at the level of 60 wt. %.

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The Analysis of Green Metrics Indices of Chemical Technologies: Accountability of Environmental Performance and Sustainability Assessments

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Abstract. *The green metrics play an important role in making the way towards the sustainability of the chemical industry. The known indices were considered in terms of environmental and sustainability input. The results of the analysis demonstrate the need for more complex types of metrics to incorporate elements of life cycle assessment, specific environmental effects, and ecological footprint.*

Keywords: reaction efficiency, environmental impacts, environmental performance, sustainability principles, circularity, ecological footprint.

Introduction

A metric is a system to provide qualitative and quantitative evaluation of processes and activities. The choice of metrics depends on the purpose of evaluation, which means that it is developed to make decisions on further actions aiming at the improvement of a process's performance. Thus, setting a clear purpose of evaluation is the key to reliable results and transforming data into valuable information. At the same time, metrics are a fundamental element for comparison of systems and technologies, different in nature, but producing the same effects. This is especially important if technological processes, like those in the chemical industry, are under consideration.

Traditionally, production and technological metrics were built on physical and chemical parameters coupled with economic indices. However, nowadays it is not enough to analyze material attributes of technologies; contemporary environmental and sustainability issues have been revealed in all types of human activity, and this calls for the development of efficient metrics to characterize these aspects of production processes.

The existing methods for evaluating products and technologies in terms of environmental impact and sustainable development are numerous and evolving. Their concepts, principles, outputs, and meanings are extremely wide. As a result, they often yield contradictory results or give fragmented characteristics of sustainability, and in particular, environmental performance. The given research aims to consider the benefits and drawbacks of existing green metrics applied to chemical processes and technologies.

Green Metrics Framework

Green metrics used in chemical technologies assessment are diverse, and there is no standard technology evaluation metric yet. The categories of metrics are different in essence and range from quantitative-subjective to qualitative, involving integration approaches quite often as well.

In particular, it is quite common to apply fundamental chemical concepts to calculate the efficiency and effectiveness of technologies. A less common approach is based on describing or rating of efficacy and safety assessment. The latter one is close to the principal needs of environmental performance and sustainability evaluation, still there is a lack of consistency in many approaches in use.

Another important distinction between metrical approaches is their point of view: metrics can be lagging or leading. The lagging approach is more common, since it is based on actual

measurements and thus it is considered to be more accurate and reliable. Environmental indicators, however, are led by their essence, and if they are applied at the project and decision-making stage, they can affect the final choices made. However, this is possible if environmental parameters are taken into consideration, which is often not the case. Sustainability indicators are also predominantly leading, and what is typical for them is that they are subject to uncertainty since the sustainability concept and principles are evolving, and cases of inconsistency and unpredictable failures are quite common. This reduces confidence in such indicators and forces researchers and decision makers to adhere to traditional computations of chemical characteristics.

There have been a considerable number of green chemistry metrics developed over the past few decades, some of the most common are: percentage yield (Y), atom economy (AE), environmental factor (E-factor), reaction mass efficiency (RME), process mass intensity (PMI), mass intensity (MI), carbon efficiency (CE), atom utilization (AU), environmental quotient (EQ), green aspiration level (GAL), relative process greenness (RPG) [1, 2].

By essence, most of these parameters refer to the correlation between the final product mass and the mass of inputs into the reaction process: reagents, catalyst, reactive environment, energy, solvents, etc. It is quite a simple and representative approach: the less mass of material used and lost or not incorporated into the final product, the lower the environmental footprint of the process is. Indices like Atom economy, E-factor, yield, reaction mass efficiency, and effective mass efficiency are examples of this impact-based metrics. With all their benefits, this group of metrics lacks important information from the environmental perspective – differentiation between hazard levels attributed to both input and output materials. Since most bulk producers of chemicals use mass-based approaches as a viable measure of their efficiency, a simple addition of the toxicity parameter to their metrics approach would significantly improve the quality of information derived from these indices and shift companies closer to real environmental performance assessment.

Actually, well-provided information is an important advantage of mass-based metrics, since it is derived from available data measured in real conditions, and minimal subjective opinions are involved. As such, it must be kept as a core of environmental and sustainability metrics to facilitate the work on the reduction of technology or process ecological footprint and overall monitoring of its environmental impacts.

Environmental and other types of sustainability aspects are better shaped for the application of impact-based metrics by essence and by providing a better basis for comparison. This is currently done via life-cycle assessment, but it is not very suitable for chemical companies producing only a limited assortment of chemical building blocks. The environmental efficiency, in its turn, is measured by counting the contribution of all processes and substances involved in climate change, acidification, ozone depletion, and formation. An intermediate approach is the calculation of the process and technology water and carbon footprint, or integrated ecological footprint. Of course, these methods are limited by the complexity of calculations, availability, and accuracy of raw data. This drawback is currently not manageable since, in many cases, specific parameters of substances' environmental profile, like ozone formation potential or acidification potential, for example, are not yet established as such research work needs considerable resources and time. With this limitation, assessment of environmental parameters as a process metric could be compromised by assumptions and analogues introduced into the assessment. This could be solved by evaluation of waste and pollution produced, scaled to some indicator substances, or measuring the volumes of non-renewable resources in the process. This again brings us to environmental impact assessment driven by inputs or outputs of the process: inputs reflect the use

of natural resources, and outputs try to measure or predict generated waste, emissions, discharges, etc. In other words, input metrics primarily characterize the sources of impacts (land and water use, energy consumed or embodied), while output metrics covers the consequences – how the processes and technologies may affect natural ecosystems, human health, and environmental values on the whole (cause generation of GHGs, ozone, acidity, eutrophication, health effects). Among the list of output parameters, human health is the most comprehensively studied, but it should be avoided as a single target parameter, since impacts on ecosystem balance have a profound effect on other living organisms and eventually destroy the human living environment, leading to health damage again.

Issues of Environmental and Sustainability Metrics Implementation

Environmental performance is an important goal of chemical metrics, but it is one of the sustainability components, as important as the economic and social profile of technology. If economic parameters are efficiently measured at the stage of the product design process, social factors are omitted in all types of metrics currently in use. The reason for this is that social metrics are hard to define and quantify, as well as find a reference system for consistent comparison [3]. In a certain way, avoidance of environmental pollution is the way to the provision of environmental equality and equity. Another indirect element of social metrics is the use of limited resources, which puts pressure on limited materials, which might cause strain in society due to limited access to them. Thus, the quantity of materials whose reserves are running out in nature is a factor to be accounted for in metrics.

The indices of sustainability offered now also tend to be mass-based, being actually the modifications of resource-waste relationships. In particular, Renewables Intensity Index and Waste Intensity Index are of this type. Being quite informative about the circularity of the processes, they still omit the other dimensions of environmental quality and sustainability.

Thus, simple quantitative mass-based and source-based metrics cannot provide comprehensive characteristics of the process and technology sustainability. Simplicity is a virtue, but it does not provide a substantiated foundation for clear comparison and decision making. As a result, there is a need to shift to integrated indices, which inevitably need more time and research for application, but leave fewer voids in the resulting evaluation.

The framework of the integrated metrics application involves climbing the levels of complexity. The first level is material efficiency or mass balance metrics, covered by most indices discussed above. At the second level, the technology's components and reagents at the input and output points are evaluated in terms of their environmental safety. The next level is applicable to the technology at the scale of industrial process, when its compliance with regulations or conformance with industrial performance standards (e.g., output concentration of hazardous chemicals versus state threshold levels and limits of waste generated) is evaluated. This is routinely done for the whole enterprise as a group of sources of pollution. Being reflective about the effect on the environment, these parameters are not applicable as elements of green metrics, since they depend on state regulations and approaches to environmental control, set by the policymakers. Moreover, they are not bound to a specific technology; rather, they characterize the overall efficiency of production at the enterprise and the applied nature protection policy.

The advanced level of metrics, which is actually able to link exact chemical processes to the environment degradation and subsequent reduction of community living standards, is when the potential contribution of the technology to the positive dynamics of eutrophication, local air quality trends, and carbon emission cost of production.

Altogether, 1-3 levels of metrics are embedded into lifecycle assessment, which traces the real footprint of the technology, starting from raw materials used to generate reactive components, their transportation, energy, and water fed into the process, and equipment used. This is also too bulky to be used as an indicative metric when technologies are compared and rated, since multiple and diverse assumptions are involved in the assessment. However, this element shouldn't be omitted; rather, its general principles should be applied to measure environmental aspects outside the reaction batch, before everything gets inside and the process starts. In a certain way, this lagging or retrospective look has much to say about the ecological footprint of the process. At the same time, it is possible to involve leading metrics elements by accounting for the lifetime of equipment and the recyclability of solvents and auxiliary materials, which is basically the next level of metrics. Thus, it is obvious that there is a need for more complex approaches to green metrics for chemical processes and technologies.

Approaching Efficient Integrated Metrics

The development of better metrics inevitably leads to the complication of metrics. At the same time, it must still be applicable, meaning it should be manageable by designers of chemical processes and technologies without long and detailed research work involved. Such developments as Green Aspiration Level [4] and CHEM 21 toolkit [5] provide a very complete picture of chemical technologies' environmental profile and sustainability, but they also represent the cases of tasks, which need specially allocated resources and time.

Overall, efficient indicators must be reliable, that is, based on real, measurable data, sensitive to minor differences between comparable systems, and rely on accessible information. The latter one can be a special problem, since information about sustainability aspects is not clearly defined, lacking, or has a fragmented character. The most well-defined is the toxicity profile for substances, but when it comes to innovative technologies, there might be completely new entries, for which relevant safety levels are confirmed for humans based on animal studies, but environmental hazards are not considered yet. In such a case, standard approaches like analogues and the biological activity of chemical bonds can be of use.

The other boundary, which sets the framework for integrated indices, is their understandability by users with minimal environmental background and clear interpretation of the results obtained. There we come back to the purpose of the green metrics. It was initially created and further amended with new indices providing better perspectives and valuations from the point of the Green Chemistry Principles, which have adapted the need to provide environmental process efficiency and reduction of negative externalities. However, most of the metrics provided cover some of the principles, and those that attempt to cover all of them are not numerous, but they should be the target for further research. In particular, EcoScale by Van Aken et al., Green Star, Color-Likert scale with hybrid assessment approach from Morales-Galicia et al., iSUSTAIN® tool, and Green Synthesis procedure by Duarte et al. are successful examples of such an approach. Most of them use a combination of mass-based, impact-based, and lagging/leading metrics, providing a good final perspective. However, most of them were developed over 10 years ago, and there is a demand for a new approach. The review of the green metrics performed by Martinez et al. [6] shows no improvements since that time, while the approaches to measuring sustainability and environmental performance have evolved considerably.

As a result, our idea is that such metrics shouldn't follow only the Green Chemistry Principles, but include at least 3 additional environmental and sustainability parameters:

1. The index of specific environmental effect – ozone depletion/generation potential, acidification potential, eutrophication potential, if they are available, and if not, the methodology

must include provisions to account for the absence of this effect, different from the score in case of the absence of information about the related effect

2. Carbon generation profile for at least two steps before and after the process itself, which is in line with current European approaches to the evaluation and notification about carbon footprint. This will be the implementation of lifecycle assessment, able to reveal hidden effects of industrial processes. Additionally, the water footprint of the process could be applied separately from the direct reagents and resources involved.

3. Sustainability assessment via the circularity potential of all components of the process. This is partially provided by the Renewables Intensity Index, which should be extended to cover equipment and materials outside the chemical process itself.

These suggestions represent the first approach to the solution of the problem and represent the pathways for further research and the search for more holistic environmental and sustainability metrics for the chemical industry. The absence of a single, formalized, and generally accepted methodology complicates development towards SDGs and increases risks of maldecisions [7].

Conclusions

Since the complete elimination of all negative externalities of chemical processes in the form of environmental impacts and sustainability barriers is impossible at the given level of technologies, the development of concise and reliable green metrics for comparative analysis and choosing the best chemical technologies is an urgent need. The analysis of the currently developed indices showed that most of them do not approach the environmental aspect of technologies beyond mass and energy efficiency. This requires the introduction of more complex parameter, which accounts for environmental and sustainability issues directly and adequately. The potential for specific environmental effects, carbon and water footprint, as well as circulation potential, were offered as amendments to the existing approaches, which assess all principles of Green Chemistry.

The practice of creating and using metrics demonstrates high flexibility in terms of measures, data sources, and instruments that they use. It might be some simple and short-lived, others highly complex and durable over an extended time frame, and therefore using different units and scales.

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Comparison of Selected Physicochemical Properties of Green Clay After Mechanochemical Treatment with the Finished Composite Based on Green Clay and Hydroxyapatite Obtained by the Wet Method

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Abstract. *Green clay and hydroxyapatite are inexpensive and readily available components for the synthesis of new, multifunctional composites. The obtained products were characterized using Fourier transform infrared spectroscopy (FTIR). Additionally, the potential value was determined. Nitrogen adsorption and desorption studies were also carried out to analyze the properties of porous composites.*

Keywords: Green clay, hydroxyapatite, montmorillonite, composite, mechanochemistry, wet synthesis.

Introduction

Nanocomposites are materials that are gaining increasing interest due to their structure and functionality. Montmorillonite is the main component of green clay, belonging to the group of layered silicates with a 2:1 layered structure, named after its origin in the vicinity of Montmorillon in France. The surface exhibits good cation exchange capacity, adsorption capacity and adhesion capacity [1].

Hydroxyapatite is a naturally occurring form of calcium apatite with the formula $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$. It constitutes about 50% of bone mass and is a source of excellent osteointegration and osteoconductive properties. It is resistant to compressive loads, and the macroporosity of its pores allows for the multiple use of its mechanical properties. Promising results are obtained both by packing hydroxyapatite into other molecules and by combining hydroxyapatite with molecules penetrating its spongy structures [2].

Experimental section

Composites 1, 2 (Table 1) were obtained using a knife mill with a mass capacity of 400 g and a speed of 24,000 rpm using the mechanochemical synthesis method. The components were weighed and ground in the knife mill for 3 minutes.

In order to obtain composite 3 (Table 1), 0.77 g of clay was measured into a flask containing 200 cm³ of distilled water, then immersed in a water bath heated to 100°C. 150 cm³ of solutions of $(\text{CH}_3\text{COO})_2\text{Ca}$ and K_2HPO_4 were placed in the dropping funnels to obtain hydroxyapatite and added dropwise over 30 minutes. The next stage of the synthesis was to boil the reaction mixture for 1 h while maintaining a constant temperature and vigorous mechanical stirring. Then the obtained precipitate was repeatedly washed with distilled water until a constant conductivity was obtained. The composite was then dried and crushed in a mortar.

Nitrogen adsorption and desorption were performed using an ASAP 2420 device from Micromeritics Inc., USA. Spectra were acquired using a Nicolet 8700A FTIR device coupled to a Thermo Scientific Nicolet NXR FT Raman spectrometer module. X-ray diffraction was recorded using an Empyrean X-ray diffractometer. Zeta potential measurements were performed using a ZetaSizer 3000 (Malvern Instruments).

Table 1

Percentage composition of samples

Sample number	Green clay [%]	Green clay burned out at 200°C [%]	Hydroxyapatite [%]
1	100	-	-
2	-	100	-
3	50	-	50

Porosimetry

The specific surface area was varied; it can be seen that for a single green clay component, the surface area was 39-42% larger than the finished composite obtained by the wet method. However, the pore volume was doubled, while the pore size increased even three times (Table 2, Figure 1-3).

Table 2

Surface testing

Sample number	Surface Area [m ² /g]	Pore Volume [cm ³ /g]	Pore Size [nm]
1	34.4	0.05	5.9
2	32.7	0.05	6.3
3	19.9	0.10	20.2

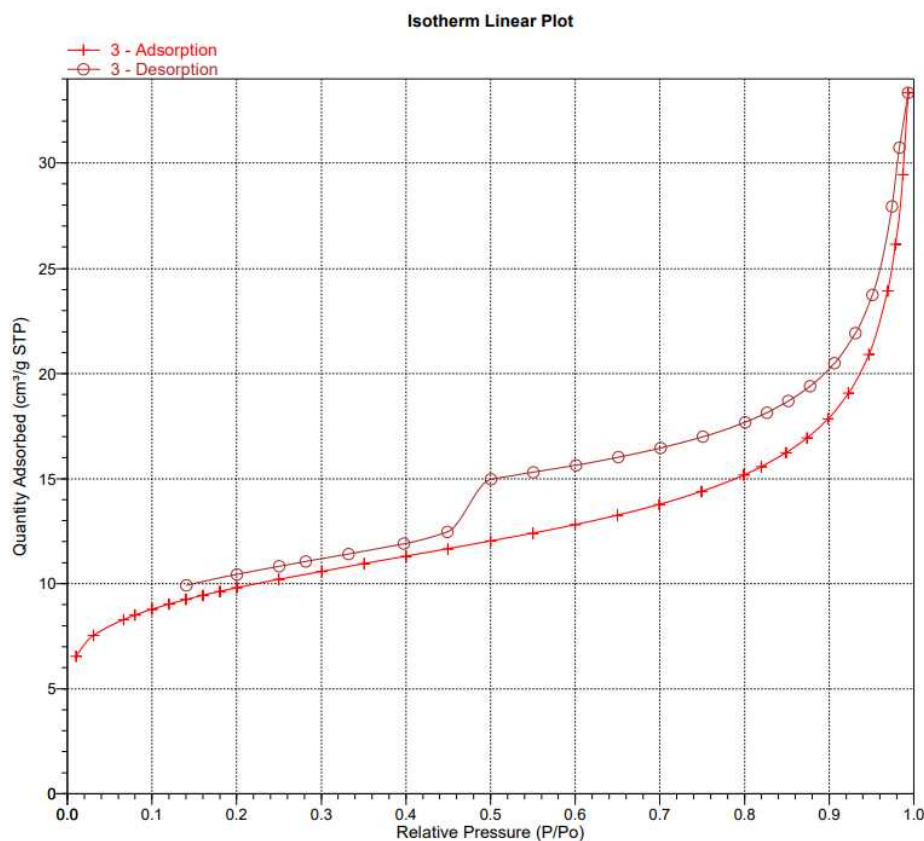


Fig.1. Isotherm linear of sample 1.

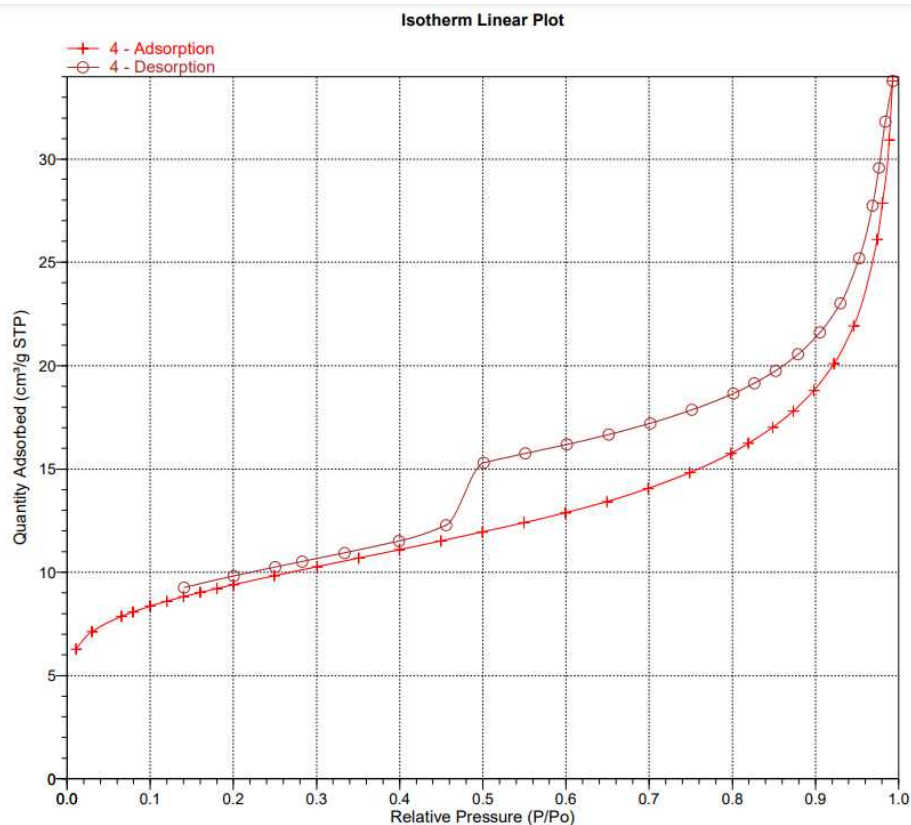


Fig.2. Isotherm linear of sample 2.

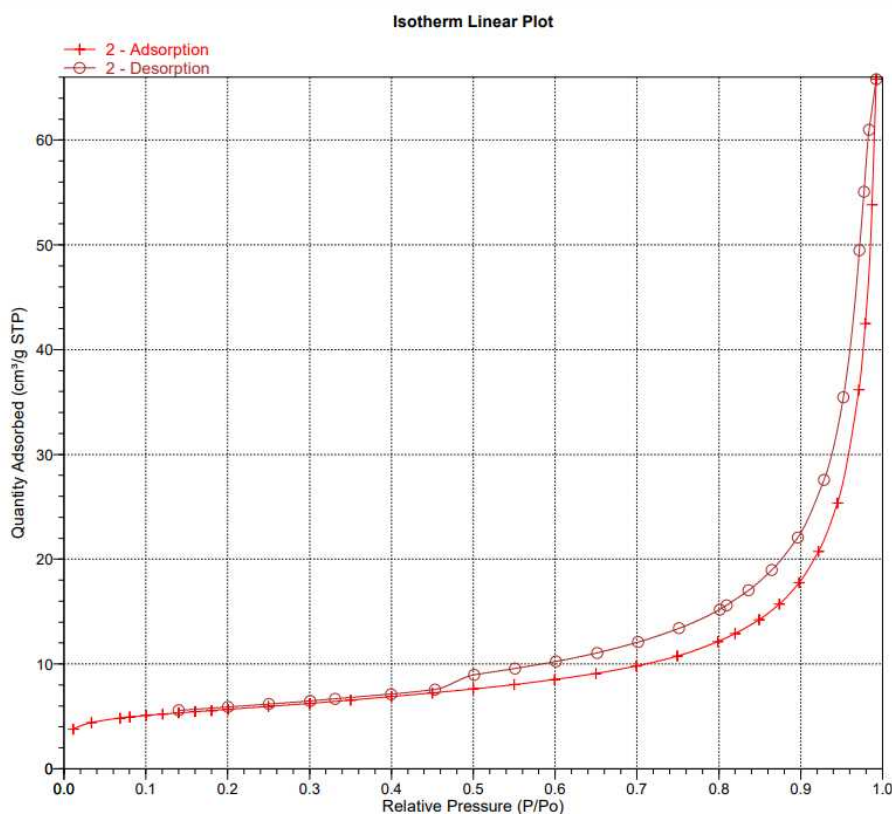


Fig.3. Isotherm linear of sample 3.

Fourier Transform Infrared Spectroscopy

We can see some differences in the spectra of the presented samples. In the spectra, we can see characteristic bands for green clay (i.e. 3621 cm⁻¹, 1115 cm⁻¹, 1031 cm⁻¹, 1039 cm⁻¹, 797 cm⁻¹,

694 cm^{-1} , 471 cm^{-1}). For sample 3 we can see bands characteristic for the presence of hydroxyapatite (1640 cm^{-1} , 1039 cm^{-1} , 471 cm^{-1}) and the presence of the -OH group (intense, broad band at 3424 cm^{-1}).

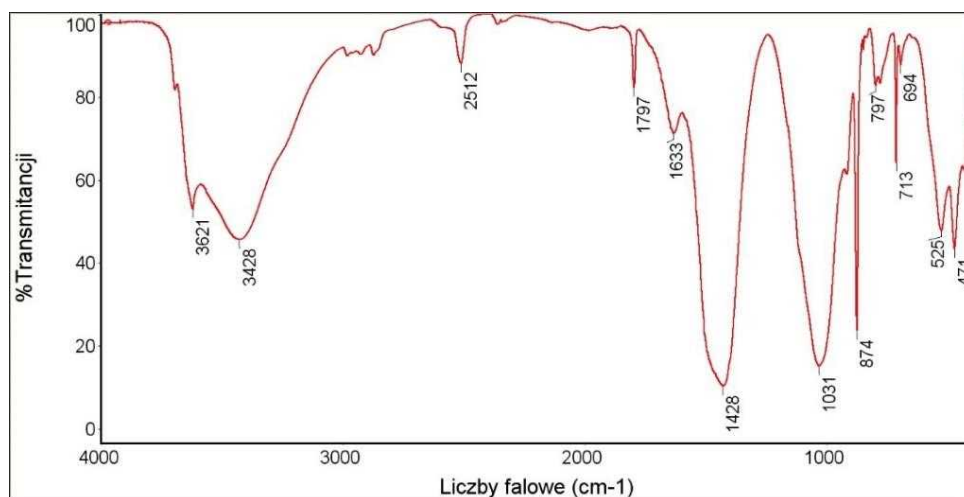


Fig. 4. FTIR spectrum of sample 1.

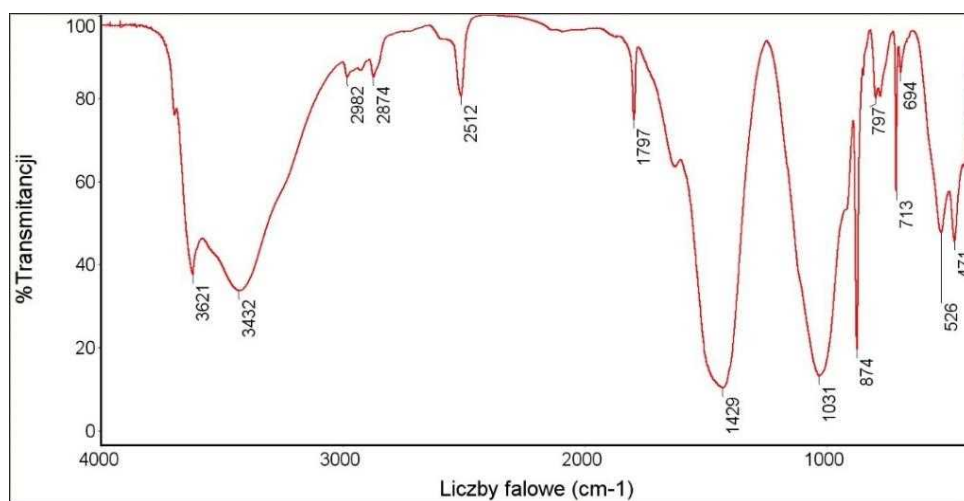


Fig. 5. FTIR spectrum of sample 2.

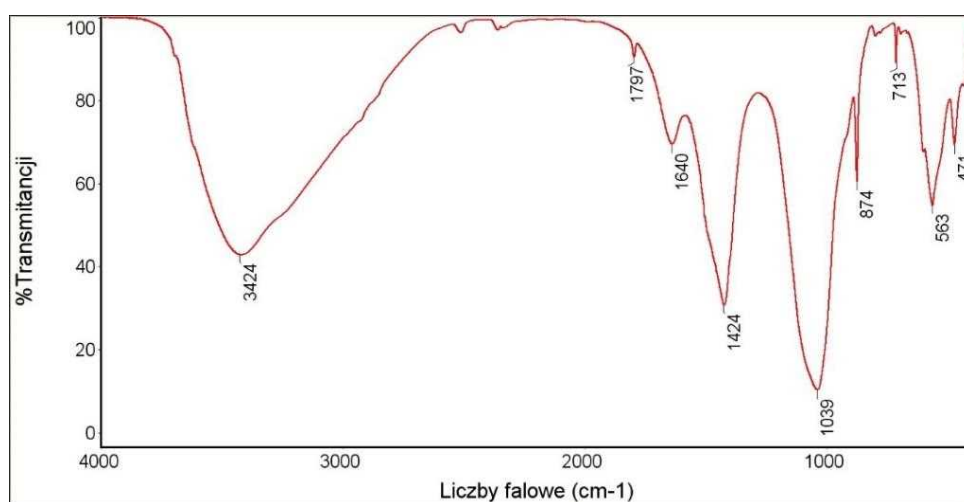


Fig. 6. FTIR spectrum of sample 3.

X-ray Diffraction

XRD studies clearly show the presence of compounds characteristic of green clay in samples 1-3, and for sample 3, also the presence of hydroxyapatite.

Lp	Ref. Code	Compound Name	Chemical Formula	SemiQuant [%]
1	04-023-8700	Calcium Carbonate	Ca (CO ₃)	60.2(4)
2	01-070-3755	Silicon Oxide	Si O ₂	28.2(3)
3	04-013-9387	Potassium Magnesium Aluminum Silicon Oxide Hydroxide	K Mg _{0.5} Al ₂ Si _{3.5} O ₁₀ (OH) ₂	11.2(4)
4	01-072-6745	Sodium Manganese Oxide Hydrate	Na _{0.364} Mn O ₂ (H ₂ O) _{0.544}	0.44(6)

Fig. 7. XRD examination of sample 1.

Lp	Ref. Code	Compound Name	Chemical Formula	SemiQuant [%]
1	04-023-8700	Calcium Carbonate	Ca (CO ₃)	60.0(4)
2	01-070-3755	Silicon Oxide	Si O ₂	28.6(3)
3	01-072-6745	Sodium Manganese Oxide Hydrate	Na _{0.364} Mn O ₂ (H ₂ O) _{0.544}	0.68(7)
4	04-013-9387	Potassium Magnesium Aluminum Silicon Oxide Hydroxide	K Mg _{0.5} Al ₂ Si _{3.5} O ₁₀ (OH) ₂	2.2(4)
5	04-016-3041	Lithium Manganese Oxide	Li Mn ₂ O ₄	0.34(7)

Fig. 8. XRD examination of sample 2.

Lp	Ref. Code	Compound Name	Chemical Formula	SemiQuant [%]
1	04-023-8700	Calcium Carbonate	Ca (CO ₃)	34.1(3)
2	01-070-3755	Silicon Oxide	Si O ₂	16.1(2)
3	00-066-0147	Calcium Phosphate Carbonate Hydroxide	Ca ₁₀ (PO ₄) _{5.63} (CO ₃) _{0.02} (OH) _{2.6}	38.1(4)
4	04-013-9387	Potassium Magnesium Aluminum Silicon Oxide Hydroxide	K Mg _{0.5} Al ₂ Si _{3.5} O ₁₀ (OH) ₂	11.7(4)

Fig. 9. XRD examination of sample 3.

Zeta Potential

The results of zeta potential measurements (Figure 10) in the pH range from 2 to 6 showed that an increase in pH in this range causes a decrease in the zeta potential value. In the pH range from 6 to 13, the results stabilize for samples 2 and 3. The tested composites were characterized by zeta potential values from 7 mV to -23 mV for sample 1 and from -10 mV to -23 mV for samples 2 and 3. The p*H*_{iep} points for sample 1 fall at about pH 4, while for samples 2 and 3, we can expect pH below 2.

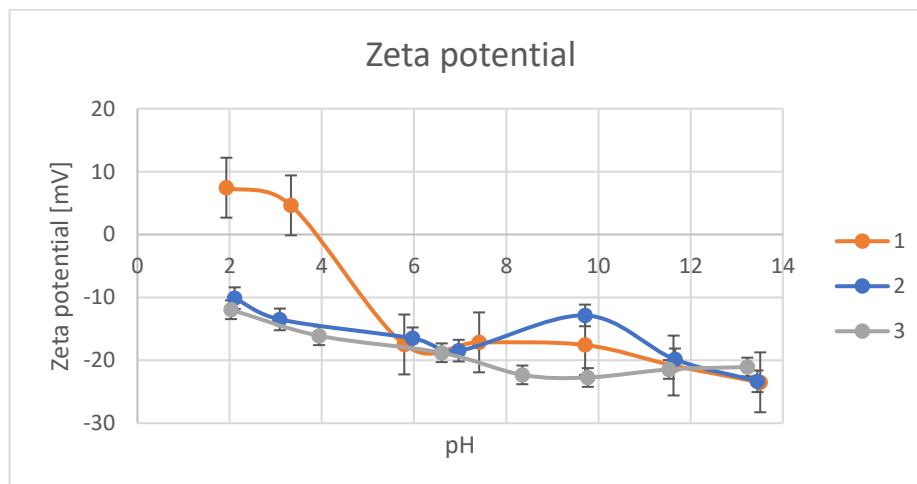


Fig. 10. Zeta potential.

Conclusions

Composites obtained by the wet method show differences in physicochemical properties. The combination of green clay with hydroxyapatite allows for an increase in the volume and availability of pores, which can significantly affect their adsorption capacity. Thanks to this, these composites can be used as carriers for bioactive compounds, expanding their potential use in medicine or materials engineering.

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Closing the Recycling Loop of PEM Electrolyzer: Synthesis of Ir Precursor from Spent Electrocatalyst

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Abstract. *This study investigates hydrometallurgical recycling of iridium (Ir) from proton exchange membrane (PEM) electrocatalyst - critical for Europe's decarbonization goals. Results demonstrate the efficient synthesis of ammonium hexachloroiridate ((NH₄)₂IrCl₆) via precipitation, which serves as a precursor for new electrocatalysts, supporting circular economy strategies in PEM electrode production.*

Keywords: proton exchange membrane water electrolysis (PEMWE), electrocatalyst, iridium, recycling, hydrometallurgy, precipitation, ammonium chloride.

Introduction

The widespread implementation of hydrogen technologies is essential for achieving a sustainable energy transition away from fossil fuel dependence [1]. Among various hydrogen production methods, water electrolysis stands out as a highly promising technology capable of efficiently generating hydrogen gas from water by utilizing renewable electricity. Electrolyzers drive electrochemical reactions, effectively converting electrical energy into chemical energy while avoiding issues related to noise and air pollution.

Among available electrolyzer technologies - such as alkaline water electrolysis (AWE), anion exchange membrane water electrolysis (AEMWE), and solid oxide electrolysis cells (SOEC) - proton exchange membrane water electrolysis (PEMWE) has emerged as particularly advantageous. PEM electrolysis offers high current densities, rapid dynamic response, and the production of highly pure hydrogen, making it especially suitable for integration with renewable energy sources [2].

The core component of the PEM electrolyzer is the membrane electrode assembly (MEA), which features catalytic layers on both the anode and cathode sides of a proton-conducting membrane. This membrane, which is usually made of perfluorosulfonic acid polymer, enables the efficient transport of protons (H⁺ ions) generated during the electrochemical reaction.

Currently, state-of-the-art PEM electrolyzers typically utilize iridium-based catalysts on the anode for the oxygen evolution reaction (OER) and platinum-based catalysts on the cathode for the hydrogen evolution reaction (HER) [3, 4]. These precious metals, however, face considerable challenges related to their scarcity, high demand, and elevated costs, driven by unique characteristics including excellent corrosion resistance, high melting points, and high densities. Consequently, platinum group metals (PGMs) have broad industrial applications beyond electrolysis, especially in the chemical industry as catalysts in processes like hydrogenation, isomerization, and steam reforming, as well as in other sectors [5].

Given the economic and environmental concerns surrounding precious metals, developing efficient recycling methods for spent electrocatalysts is imperative. Hydrometallurgy has been extensively studied and identified as a sustainable and effective approach for the recovery of PGMs. Compared to pyrometallurgical techniques, hydrometallurgy provides significant environmental advantages due to its operation at relatively low temperatures, while maintaining high recovery efficiencies. This approach typically consists of three main stages: (i) leaching the target metals using suitable aqueous media (acidic or alkaline); (ii) separating and concentrating

the metals, and (iii) recovering the target elements either in pure metallic form or as specific metal salts [5, 6].

In this work, we focus specifically on the final stage of an environmentally friendly recycling approach previously developed by our group [3, 7]. We investigate the precipitation of iridium in a form of salt $(\text{NH}_4)_2\text{IrCl}_6$ from solution obtained through hydrometallurgical recycling process of spent PEM electrocatalyst. This critical step contributes significantly toward closing the loop and achieving circularity of PGMs within the hydrogen economy.

Experimental part

Materials

The following chemicals were used for experiments and analyses: HCl (37%, VWR), H_2O_2 (30%, Merck), NH_4Cl (99.8%, Merck). The iridium salts $\text{IrCl}_3 \cdot 3\text{H}_2\text{O}$ (99.99% metal basis, Alfa Aesar) and IrCl_4 (99.95% metal basis, Thermo Scientific) were used for obtaining Ir-based solutions with different oxidation states of iridium.

The PEM electrode used for the testing was produced within the “Recycalyse” project by the Danish Technological Institute (DTI, Denmark). The electrode treatment steps described in our previous research [3, 7]. For the precipitation steps, the real or model solutions were utilized. Ir-containing model solutions were prepared using 10 000 $\mu\text{g/mL}$ standard solution of IrCl_3 in 20% HCl (99.99% Alfa Aesar). The real Ir-based electrocatalyst solutions were used after the leaching tests with HCl, and contained in addition Pt, Ru, Sb, and Sn as the side elements.

Precipitation

The Ir precipitation process was carried out by adding 5 mL ammonium chloride solution (5M NH_4Cl) to 40 mL of Ir-based solution (model or real solution with Ir starting concentration of ca. 400 mg/L) under stirring (200 rpm) at room temperature (RT). In the case of the oxidation step, 2.5 mL of 30% H_2O_2 was added to the solution and heated to 70 °C. The samples were taken after 30 min, 1h, 2h, 3h, and 24h to monitor the precipitation efficiency. The metal concentrations in the aqueous solution were quantified using inductively coupled plasma-optical emission spectrometry (ICP-OES, Varian Agilent 725-ES).

Results and discussion

For the separation of iridium, a multi-step refining procedure previously described in our work [7] was employed. This procedure includes delamination of the membrane from the catalyst layers, fusion, hydrochloric acid leaching, and solvent extraction using a Cyanex 923/diesel mixture. The solvent extraction step effectively separates Ir from accompanying elements found in the investigated electrocatalyst, such as platinum (Pt), ruthenium (Ru), antimony (Sb), and tin (Sn).

In the current study, precipitation using ammonium chloride (NH_4Cl) was performed as a final purification step to recover Ir from the aqueous phase. To synthesize the ammonium hexachloroiridate $(\text{NH}_4)_2\text{IrCl}_6$, crucial precipitation parameters - including additive concentration, precipitation temperature, and duration - were systematically optimized to achieve high precipitation efficiency.

In HCl-based solution, Ir predominantly exists in two oxidation states: Ir(III) and Ir(IV), forming complexes such as IrCl_6^{3-} and IrCl_6^{2-} or other species [8]. Therefore, evaluating precipitation efficiency as a function of the oxidation state of Ir is essential.

For solutions containing predominantly Ir(III), an additional oxidation step was tested to convert it to Ir(IV). Hydrogen peroxide (H_2O_2) was selected as an oxidizing agent, due to its ability to decompose without leaving residual impurities.

The precipitation efficiency was evaluated using 5M NH_4Cl as the precipitating agent according to Eq. 1.

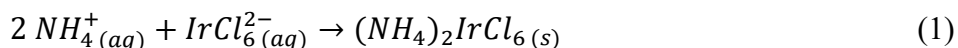


Fig. 1 illustrates the precipitation efficiency of various Ir species in both model and real solutions, with and without the addition of an oxidizing agent. The model solutions were prepared by dissolving corresponding Ir salts in 3M HCl, while the real electrocatalyst solution (denoted as cat. sol.) originated from HCl leaching of the spent electrocatalyst. As a result, it also contained other elements present in the original material (such as Pt, Ru, Sb, and Sn), which may affect Ir precipitation compared to the single-ion system. The results show that the Ir(III) species exhibit high solubility; therefore, their conversion into the less soluble Ir(IV) species is necessary for effective Ir recovery. In electrocatalyst-based solutions, partial precipitation of Ir (approximately 33.6%) suggests the coexistence of both Ir(III) and Ir(IV) species. Upon addition of the oxidizing agent, Ir recovery significantly increased, exceeding 81%.

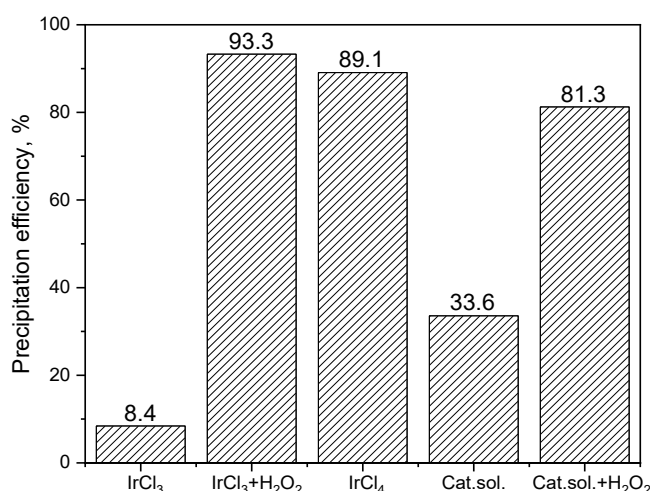


Fig. 1. Precipitation efficiencies of Ir depending on its oxidation state and type of the solution (model vs. real) after 24h at RT and 200 rpm.

Optimization of process parameters (i.e., the oxidant type, reagent concentrations, reaction time, and temperature) was conducted. A range of hydrochloric acid concentrations (1-10M HCl) was examined, with Ir recovery reaching 93.4% at 4M HCl. Notably, increasing the HCl concentration beyond 8M resulted in a stable precipitation efficiency of around 97.6%.

The purity of the recovered ammonium hexachloroiridate $(\text{NH}_4)_2\text{IrCl}_6$ was assessed, revealing an Ir content of $45.86 \pm 0.42\%$. This experimental value aligns closely with the theoretical Ir content in the salt ($\text{Ir}_{\text{theor.}} = 43.6\%$), considering an analytical error of approximately 1-2%. The purity of the final product is largely dependent on the presence of other accompanying elements. Therefore, achieving a highly purified Ir-containing solution prior to precipitation, for instance via solvent extraction methods previously developed by our research group [7], is recommended.

Further investigations are necessary to evaluate the performance of the recovered material in electrochemical applications following electrocatalyst fabrication. Nonetheless, previous experience from our studies [6] indicates that ammonium salts $(\text{NH}_4)_2\text{PtCl}_6$ and $(\text{NH}_4)_2\text{RuCl}_6$) synthesized via this method exhibit electrochemical properties comparable to commercially available precursors.

Conclusions

Due to the growing demand for iridium in the proton exchange membrane water electrolysis industry, efficient recycling techniques must be developed and tailored for new and complex materials, such as electrocatalysts.

In this study, the final precipitation step for recovering Ir from the solution of spent electrocatalyst was systematically investigated. Optimal precipitation conditions were established, identifying that the Ir(IV) oxidation state is preferable for efficient recovery. This state can be effectively attained by incorporating an oxidizing agent such as hydrogen peroxide. Under optimized conditions (5M NH_4Cl , 8M HCl , room temperature, 24 hours stirring at 200 rpm), a high recovery yield of 97.6% was achieved. The synthesized ammonium hexachloroiridate ($(\text{NH}_4)_2\text{IrCl}_6$) salt can directly serve as a precursor for electrocatalyst production, facilitating the recycling and sustainability of PGMs in PEM technology.

Acknowledgments

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Animal Fats and Vegetable Oils – Promising Resources for Obtaining Effective Corrosion Inhibitors for Oil Refinery Equipment

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Abstract. The conditions for the synthesis of new corrosion inhibitors (CIs) from distilled higher acids of beef fat or vegetable oils are considered, and the protective effect of the synthesized corrosion inhibitors in comparison with industrial inhibitors is investigated. The results prove the possibility of alternative use of animal fats and waste from their production as new resources for obtaining highly effective equipment corrosion inhibitors. Using alternative inexpensive raw materials to obtain CIs will improve the economic performance of inhibitor production.

Keywords: biological resources; corrosion inhibitor; protective effect; higher fatty acids; vegetable oil.

Introduction

The sustainable process of waste and low-quality minerals engineering, reuse, and valorization of biomass are the main directions of creating new raw materials and resource sources. This significantly increases the circular economy's role and improves the ecology of the environment.

The refining industry and other fuel industries face significant corrosion challenges due to exposure to aggressive media, including mineralized water, acids, and other corrosive components. This requires effective corrosion inhibitors to protect equipment and increase its service life. The use of inhibitors is one of the most critical and widespread corrosion control methods [1]. According to the oil companies' requirements, the inhibitors must provide maximum protective effect at a sufficiently low concentration, be technological (not to disrupt the normal technological mode of operation of the plant), and not degrade the quality of products and the operation of catalysts of secondary processes.

Given the above, it is advisable to study the production of corrosion inhibitors based on the most common vegetable oils, animal fats, or their production wastes in Ukraine and the world. Comparative tests of corrosion inhibitors from well-known companies and corrosion inhibitors

based on renewable raw materials showed a relatively high protective effect of the latter. Therefore, this work aims to continue the above experiments using amino derivatives to synthesize green corrosive inhibitors from raw plant and animal materials. Investigating their protective effects in a highly corrosive medium and comparing their efficiency with known inhibitors of world manufacturers is also necessary. Given that much of the research is devoted to synthesizing corrosion inhibitors from different types of raw materials at various temperatures, the simplest way to analyze their effectiveness (weight tests to assess the mass loss) is to select 1-3 optimal inhibitors. This will allow valorizing oils, animal fats, and waste from their production as potential raw materials for producing highly effective, inexpensive compounds used in the oil industry to reduce equipment corrosion.

Materials and Methods

To compare the protective effect of the synthesized inhibitors and those used today in oil refining, we used corrosion inhibitors manufactured by Chimec (Italy), SUEZ (France), Clariant (Switzerland), Nalco (USA), and Barva LLC (Ukraine). The active substance of inhibitors is dissolved in a hydrocarbon solvent.

The corrosion studies were performed on samples of St20 steel with a total area of 30 cm² and a rectangular shape. Diethanolamine, diaminoethanol, and triethanolamine used in the study were of 99.7% purity. Isopropyl alcohol and hydrocarbon solvent were of PA grade.

The high protective effect of corrosive inhibitors is caused by the interaction of higher fatty acids in the composition of raw materials with amines [2, 3]. That is why natural raw materials and amines were used for the synthesis. A flow diagram of the preparation of the corrosion inhibitor working solution is shown in Fig. 1.

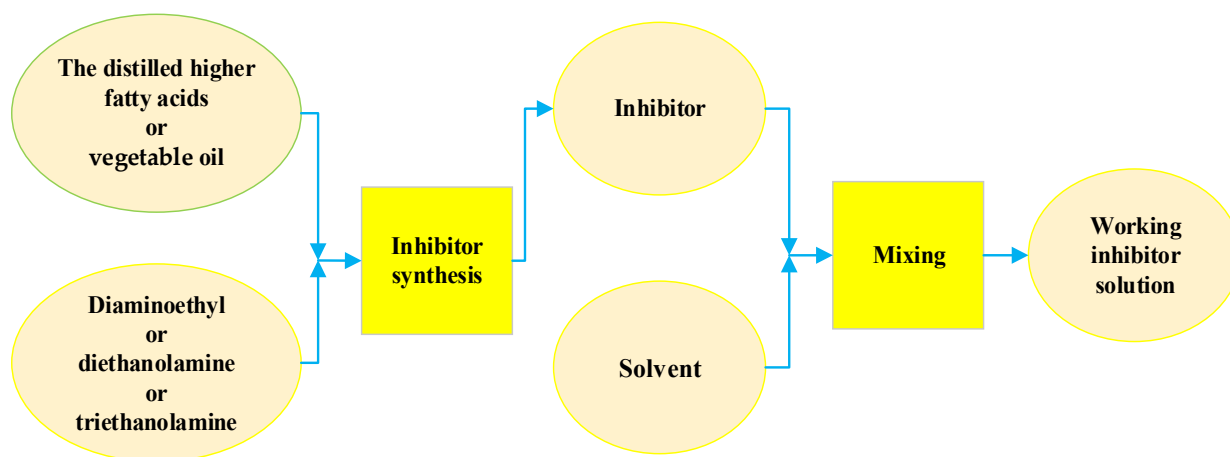
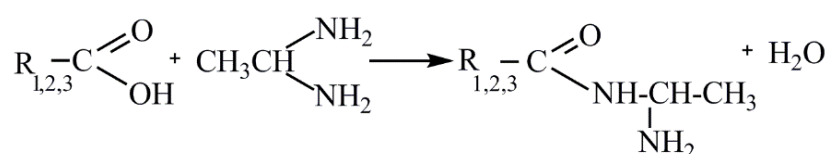
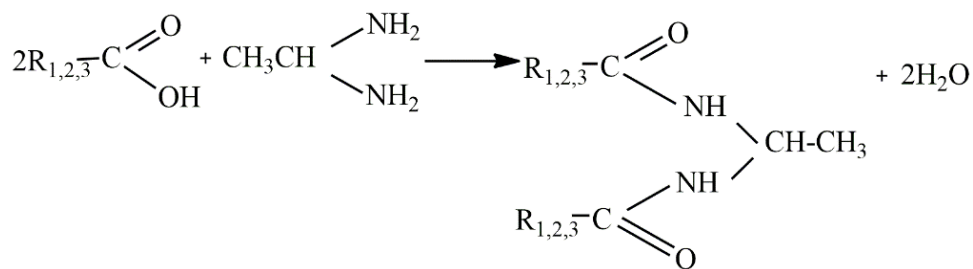


Fig. 1 Flow diagram of the preparation of the corrosion inhibitor working solution.

As a result of the reaction of acid and ethyl diamine, monosubstituted or disubstituted ethylamide can be obtained (see Scheme 1).



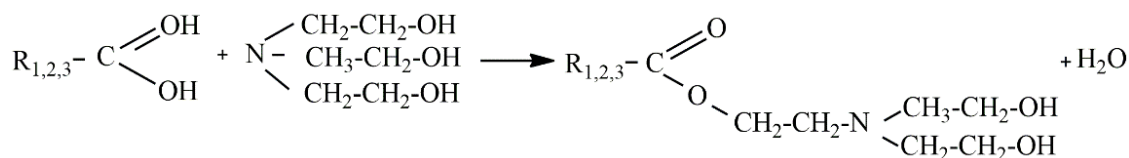
(a)



(b)

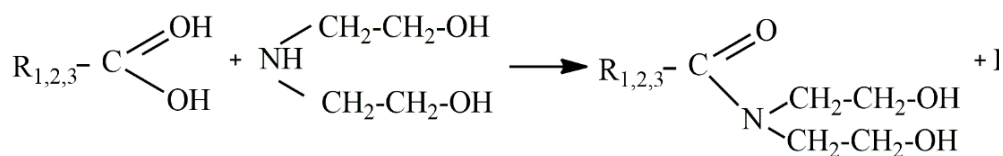
Scheme 1. Reaction of fatty acid and ethyl diamine with the production of monosubstituted (a) or disubstituted ethylamide (b): R_1 is $\text{C}_n\text{H}_{2n+1}$, R_2 is $\text{C}_n\text{H}_{2n-1}$, and R_3 is $\text{C}_n\text{H}_{2n-3}$ —fatty acid alkyl chain.

According to the results presented in this paper and our previous results, the participation of triethanolamine in the synthesis process has less impact on the protective ability of the resulting compounds. The esterification reaction prevails when fatty acids and triethanolamine interact at 130–150 °C. As a result, triethanolamine ester is formed (see Scheme 2).



Scheme 2. Reaction of fatty acids and triethanolamine with the production of triethanolamine ester: R_1 is $\text{C}_n\text{H}_{2n+1}$, R_2 is $\text{C}_n\text{H}_{2n-1}$, and R_3 is $\text{C}_n\text{H}_{2n-3}$ —fatty acid alkyl chain.

The reaction of DHFA and diethanolamine has a more significant effect due to the formation of dihydroxyethylamide of higher fatty acids (see Scheme 3).



Scheme 3. Reaction of fatty acids and diethanolamine with the production of dihydroxyethylamide: R_1 is $\text{C}_n\text{H}_{2n+1}$, R_2 is $\text{C}_n\text{H}_{2n-1}$, and R_3 is $\text{C}_n\text{H}_{2n-3}$ —fatty acid alkyl chain.

Thus, the synthesized inhibitors act on the principle of forming a multilayer protective film consisting of the polar and hydrophobic layers. As mentioned above, there are various approaches to analyzing the degree of corrosion and the effectiveness of inhibitors. The gravimetric method determined the inhibitor effect based on our developed methodology [4], which consists of determining the weight loss of a metal plate arranged in the medium with and without an inhibitor.

The two-phase medium consisted of an aqueous salt solution and jet fuel. The composition of the aqueous salt solution was as follows: NaCl - 163 g/L, $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ - 17 g/L, $\text{Ca}(\text{HSO}_4)_2 \cdot 2\text{H}_2\text{O}$ - 0.14 g/L, CaCl_2 - 34 g/L. The water: jet fuel ratio was 1:9 (wt/wt). This medium simulates water formation in oil production facilities or the corrosive environment formed in water tanks after electric dehydrators.

The inhibitor introduced into the medium was 100 and 200 ppm of the active substance. Under the experimental conditions, this amounted to 0.65 mL and 1.3 mL of a 5% working inhibitor solution per 300 mL medium.

Figure 2 shows the laboratory setup for the investigation of the inhibitor effect. A magnetic stirrer heating element and a contact thermometer regulated and maintained the process temperature within the specified limits. The mixing intensity was controlled by changing the rotation speed of the magnetic stirrer.

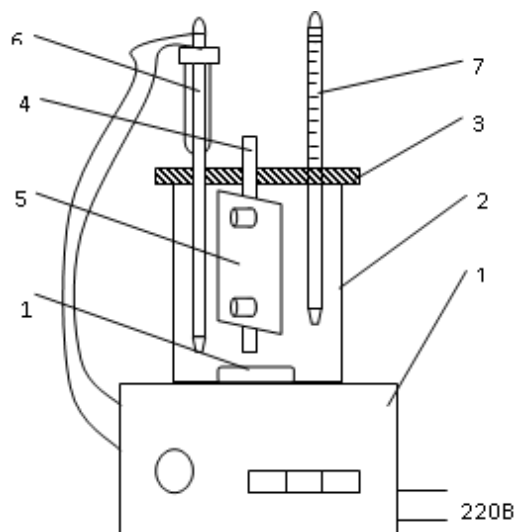


Fig. 2. Setup for studying the anticorrosive ability of inhibitors using the gravimetric method.

1 - magnetic stirrer; 2 - chemical beaker; 3 - teflon lid; 4 - glass rod; 5 - metal plate; 6 - contact thermometer; 7 – thermometer.

Quantitative assessment of the inhibitor effect (at a specific concentration) on the rate of the corrosion process is characterized by the protective effect Z , which was determined at temperatures of 50, 60, and 70 °C. The protective effect Z is the ratio of the difference in metal corrosion rates in the media without and with an inhibitor to the metal corrosion rate in an aggressive medium without an inhibitor, expressed as a percentage:

$$Z = \frac{V_0 - V}{V_0} \cdot 100 \quad (1)$$

where V_0 is the metal corrosion rate in an aggressive environment, $\text{g}/(\text{m}^2 \cdot \text{h})$, and V is the metal corrosion rate after the addition of inhibitor, $\text{g}/(\text{m}^2 \cdot \text{h})$.

Corrosion rate V (V_0) [$\text{g}/(\text{m}^2 \cdot \text{h})$] was determined as the ratio of the plate weight loss due to corrosion to the plate surface area over a certain period:

$$V (V_0) = \Delta m / (S \cdot t), \quad (2)$$

where Δm is the decrease in the metal plate weight due to corrosion, [g]; t is the time of the experiment, [h], equal to 2 hours; S is the surface area of the metal plate, [m^2], equal to 0.003 m^2

To confirm the reliability of the results obtained, the protective effect of inhibitors under certain conditions was determined 3 times using this method. The deviation of the values of the obtained results was no more than 5%, confirming these studies' reproducibility. The average value for each survey was taken as accurate.

The surface microstructure of the studied plates covered with a layer of inhibitor and without it was carried out on a desktop scanning electron microscope CEN NeoScop (Japan). For the study of corrosion inhibitors, an accelerating voltage of about 10 kV was chosen to ensure an optimal balance between image detail and surface integrity. The surface samples were magnified 5000 times.

Results

The protective effect Z was determined at a temperature of 50 °C. This temperature is typical for refinery equipment exposed to corrosive media. Thus, the coconut oil-based inhibitor provides long-term protection of metal surfaces through a combination of hydrophobicity and adsorption ability. This is practically the level of effect shown by sunflower oil (cf. 71.3%).

So, it is evident that the protective effect of inhibitors synthesized from vegetable oils and triethanolamine strongly depends on the synthesis temperature; for sunflower oil, the maximum impact is achieved at the synthesis temperature of 140 °C; for corn and coconut oils – at 130 °C.

Therefore, for each type of oil, the efficiency of the inhibitor is achieved at certain synthesis temperatures, which may indicate the optimal ratio between the polar and nonpolar parts of the molecules that form a stable film.

The effect of synthesis temperature on the quality of DHFA-based inhibitors is similar to that of vegetable oil-based inhibitors:

- with increasing temperature, the density (and, accordingly, the molecular weight) of the products increases;
- the temperature of 130°C is optimal for achieving maximum molecular activity, which contributes to forming a stable protective film.

The surface microstructure of the studied plates was studied using an electron microscope at a magnification of 5000 times.

At a magnification of 5000 times, it is seen that the surface of the plate, which was in an environment without an inhibitor, is uniformly corroded. At the same time, even the surface of the metal, which was exposed to the air, was corroded. When the synthesized inhibitor is introduced into the environment, the surface of the plate looks solid without corrosion damage

Notably, the degree of protection of the synthesized inhibitor is relatively high and close to the degree of protection of the industrial corrosion inhibitor Dodigen 481.

Finally, the environmental and economic aspects of the work should be considered. Using alternative natural resources will allow the utilization of animal waste and the production of bio-friendly compounds, and provide a significant economic impact. This, in turn, makes it attractive to introduce large-scale production and use of the corrosion inhibitors under study

Conclusions

This study emphasizes the prospects of using inhibitors based on organic raw materials in the industry, which contributes to the development of sustainable technologies and compliance with environmental requirements. New corrosive inhibitors based on natural raw materials were obtained under different conditions and with varying ratios of the components. The inhibitors synthesized from vegetable oils and triethanolamine were found to have a slight protective effect against metal corrosion compared with inhibitors based on distilled higher fatty acids derived from beef fat and diethanolamine. The best results were obtained for the sample with DHFA: amine ratio of 72:28 (wt/wt) synthesized at a temperature of 130 °C and time of 4 hours. It demonstrates a 99% protective effect at the corrosive medium temperature of 50 °C. The increase in temperature to 70 °C slightly decreases the impact to 95.6 %.

Studies have shown that the content of unsaturated compounds in the feedstock of plant origin has virtually no effect on the protective properties of the synthesized compounds. Therefore, vegetable oils can also be a promising raw material for producing N-containing corrosion

inhibitors in the case of obtaining amides based on them. Thus, future research will aim to achieve higher protective properties of compounds synthesized based on Ukraine's most common vegetable oils (e.g., sunflower, rapeseed) and diethanolamine.

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ALTERNATIVE AND NON-CONVENTIONAL ENERGY SOURCES

The Characteristics of Banana Peel-Derived Carbon and Its Potential Utility in Energy Storage Devices

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Abstract. *The main aim of this work is to present banana peel hard carbon as a candidate for electrode material for electrochemical power sources. The test yielded a capacitance of $\sim 50 \text{ F g}^{-1}$ for the supercapacitor and perfect cyclic reversibility.*

Keywords: carbon, banana peel, kinetics, capacitor.

Introduction

In recent decades, scientists have placed increasing emphasis on studying the detrimental effects of global warming and increasing greenhouse gas emissions on everyday living conditions. Studies conducted highlight that human activities over the years have severely affected environmental conditions, food production and water availability, with little or no improvement predicted [1]. Issues such as ozone depletion and rising sea levels have negatively affected agriculture, leading to inadequate and poor quality nutrition, which indirectly harms human health. We are faced with a key challenge: while the demand for electricity continues to grow with advances in technology, it has become necessary to look for greener alternatives, in particular to replace traditional and electrochemical energy sources. It is therefore becoming evident that there is increasing pressure to develop environmentally friendly energy storage solutions. According to the principles of 'Green Chemistry', the degradation processes of the materials used during the process must be designed correctly. The use of carbon-based biomaterials can help to reduce the environmental impact during the manufacture of cells and capacitors. These materials have unique chemical and electrochemical properties that enable efficient charge collection and transfer in energy storage devices. Both the production and disposal of batteries and supercapacitors still involve numerous environmental challenges, despite the fact that their use has already become commonplace in today's modern technologies. In this context, banana peels represent an interesting waste raw material that can be transformed into a functional carbon material through a carbonisation process. The carbonisation process, carried out under controlled conditions, makes it possible to obtain a material with a specific chemical structure, which is crucial for its potential applications.

Preparation of carbon materials and measurement systems

Banana peel was used during this study. Carbonisation of the material was carried out at a temperature of 600°C. Electrochemical measurements were carried out using the systems shown in Figure 1.

Physicochemical properties of the obtained materials

To understand the basic structure of the carbon material obtained from banana peel carbonised at 600°C, FTIR, XRD and TG/DTG-DTA analysis was performed.

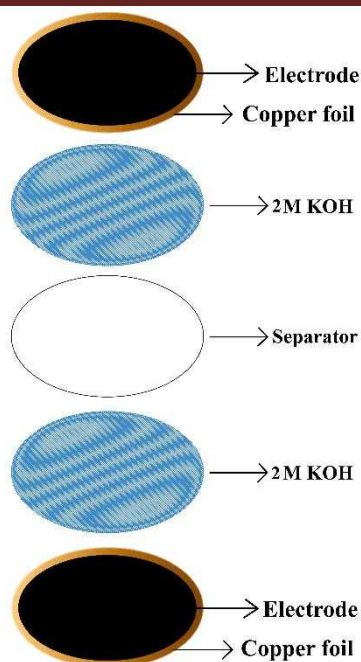
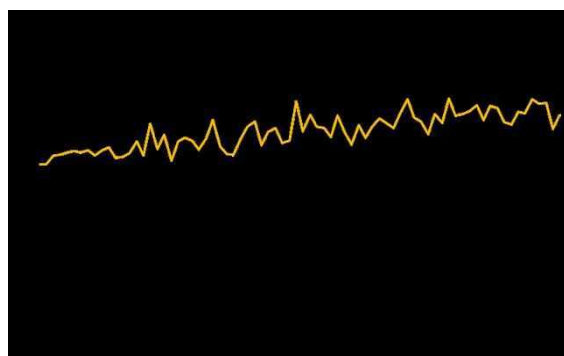


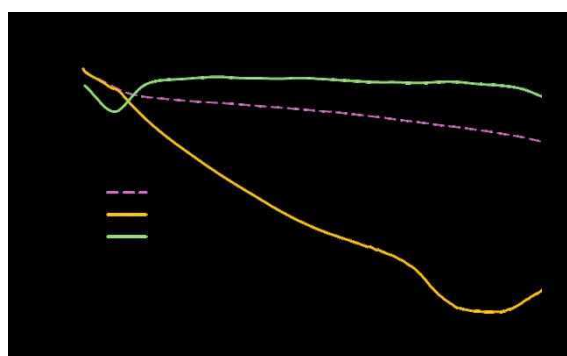
Fig. 1. Scheme for capacitor: electrode | 2M KOH | electrode.



(a)



(b)



(c)

Fig. 2. Diagrams for (a) FTIR; (b) XRD; (c) TGA/DTA.

The FTIR plot (Fig. 2a) shows broad transmittance minima in the region of wave number values $3400\text{--}3000\text{ cm}^{-1}$, which is typical of stretching vibrations of hydroxyl (O-H) groups. The $3000\text{--}2800\text{ cm}^{-1}$ region is characterised by signals associated with stretching of C-H bonds in methyl groups and methylene groups ($-\text{CH}_3$ and $=\text{CH}_2$). This is due to the pyrolysis process, during which the original organic structures are transformed into more aromatic and condensed structures. The $2400\text{--}2200\text{ cm}^{-1}$ region, with a clear transmittance minimum, suggests the presence of $\text{C}\equiv\text{C}$ or $\text{C}\equiv\text{N}$ bonds. A marked decrease in transmittance in the range

1700-1600 cm^{-1} corresponds to stretching vibrations of carbonyl groups ($\text{C}=\text{O}$), usually associated with ketones, esters or carboxylic acids [2].

The XRD plot (Fig. 2b) shows the structural characteristics of the carbonaceous material obtained by carbonisation of banana peel at 600°C. Analysing its shape, broad and fuzzy bands instead of sharp peaks can be observed, indicating a largely amorphous structure of the material obtained. Typical for biomass-derived carbons, the diffraction maximum around $23^\circ 2\theta$, attributed to the (002) plane of graphitic carbon, is poorly formed, indicating a low degree of order in the structure of the carbon layers. A second broad band around $43^\circ 2\theta$, associated with plane (100), suggests the presence of a short ordering in the carbon structure [3]. Under such conditions, full dehydroxylation and reorganisation of the structure towards well-ordered graphitic domains does not occur, resulting in carbon with a high degree of amorphisation.

The curves (Fig. 2c) illustrate a gradual weight loss that starts as early as below 200°C, which can be related to the evaporation of volatile compounds. At higher temperatures, material degradation becomes more intense. Burning of organic components occurs intensively in the temperature range of 200-700°C.

Data obtained by TG analysis were used to determine kinetic parameters using the Coats-Redfern (CR) method [4]. The activation energy (E_a) and pre-exponential factor (A) were calculated, based on the assumption of a first-order reaction. The graphical representation of the relationships allowed a linear fit to the data and determination of kinetic parameters such as enthalpy change, entropy and free enthalpy. The results obtained are shown in Table 1.

Table 1

Thermodynamic and kinetic parameters of banana peel carbon degradation

Parameter	Carbon material
E_a (kJ mol^{-1})	30.4
A (min^{-1})	113024
$\ln A$ (a.u.)	11.64
k (min^{-1})	$9.52 \cdot 10^{-2}$
ΔG (kJ mol^{-1})	101.4
$\Delta H=Q_p$ (kJ mol^{-1})	27.6
ΔS ($\text{J mol}^{-1} \text{K}^{-1}$)	-218
K (a.u.)	$2.25 \cdot 10^{-16}$

The value of the activation energy (E_a) is 30 kJ mol^{-1} is relatively low. The enthalpy change is 28 kJ mol^{-1} . The value of ΔG is positive, indicating a forced process. The negative value of ΔS indicates an increase in the degree of ordering of the system during the reaction, which is probably related to the ordering of structures and condensation processes during the formation of carbon structures.

Electrochemical properties of the material obtained

Electrodes based on the carbon materials obtained were subjected to cyclic voltammetry (CV) analysis (Fig. 3).

The curves do not show the 'rectangular' shape classic of electrochemical capacitors. The more rounded shape may be due to the presence of pseudo-capacitive reactions. The current density in the system increases with scanning speed, yet the trends of the curves remain consistent. The electrode material appears to be stable, due to the lack of deviation after many cycles of operation.

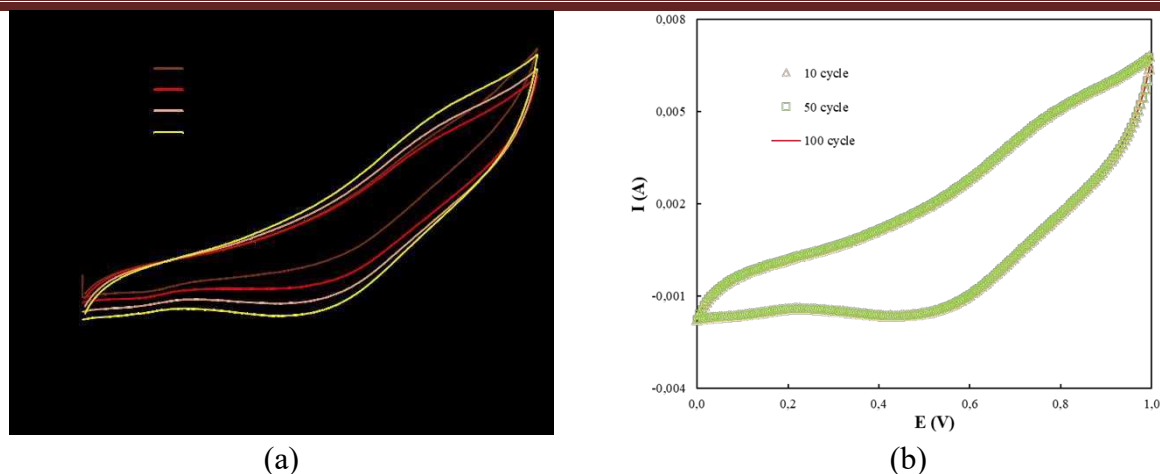


Fig. 3. Cyclic voltammetry curves for system: electrode | 2M KOH | electrode capacitor (a) for different scan rates; (b) for scan rate of 5 mV s^{-1} and different number of cycles.

Conclusions

Physicochemical analysis indicates that the structure of banana peel-derived carbons has a significant impact on their potential use in energy storage devices. The most important point remains that the process of obtaining the material is endothermic, which makes it possible to believe that the degradation processes of the material will not have a significant impact on the performance of capacitors.

Banana peel offers an economical and environmentally friendly alternative to conventional activated carbon, reducing production costs while maintaining high carbon content and performance benefits. Banana peel-based electrodes exhibit excellent redox reversibility and high stability, with significant charge storage capacities (approx. 50 F g^{-1} in supercapacitors).

Acknowledgments

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Methods of Biogas Purification and Enhancement

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Abstract. *This review explores the advancements in biomethane production, focusing on biogas purification techniques and CO₂ methanation methods. Key technologies are analyzed for their efficiency and sustainability. The study highlights innovative approaches for integrating renewable hydrogen into methanation processes, offering solutions for carbon neutrality and energy transition.*

Keywords: Biomethane, biogas, purification, hydrogen sulfide, carbone dioxide, CO₂ methanation.

Introduction

Biomethane production has gained significant attention in recent years due to its potential as a renewable energy source that contributes to carbon neutrality. Biomethane, a purified form of biogas, can be used as a substitute for natural gas in various applications, including heating, electricity generation, and as vehicle fuel. However, biogas in its raw form contains impurities such as hydrogen sulfide (H₂S), carbon dioxide (CO₂), and other trace gases that need to be removed to produce high-quality biomethane.

The importance of biomethane production is underscored by its role in achieving global energy transition goals and reducing greenhouse gas emissions. Regulatory frameworks such as the Paris Agreement, the European Green Deal, and Ukraine's National Energy and Climate Plan emphasize the need for sustainable energy solutions, including the production and utilization of biomethane.

Biomethane has diverse applications, including its use as a clean fuel for vehicles, a reliable energy source for industrial processes, and a means of decentralizing energy production. Additionally, the by-products of biomethane production, such as digestate, can serve as valuable fertilizers, promoting circular economy practices. The growing interest in biomethane is also driven by its potential to replace natural gas in existing infrastructure, offering a seamless transition to renewable energy.

Our previous review [1] was devoted to the purification of gases from hydrogen sulfide. This article **aims** to provide an overview of existing methods and recent advances in biogas purification from both hydrogen sulfide and carbon dioxide and biomethanization.

With the growing need for sustainable energy solutions, advancements in technology have further enhanced the efficiency and feasibility of biomethane production. A deeper understanding of purification methods, alongside the integration of renewable hydrogen for methanation, provides opportunities to address global energy and environmental challenges.

Results and Discussion

1.1 Methods and Studies on Hydrogen Sulfide Removal

Hydrogen sulfide (H₂S) is a toxic and corrosive gas that must be effectively removed from biogas [1-9]. The key chemical reactions and corresponding technological schemes for H₂S removal are as follows:

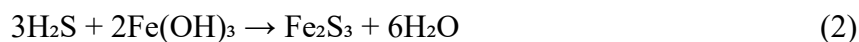
1.1 Chemical Scrubbing

Chemical scrubbing involves the use of alkaline solutions such as sodium hydroxide (NaOH) or iron-based compounds to react with H₂S. Recent studies have highlighted the

efficiency of using iron chelates, which form stable precipitates with H_2S , achieving removal efficiencies exceeding 99% [1]. However, the high operational costs and disposal of spent chemicals are significant drawbacks.

Further advancements include the development of hybrid systems combining chemical scrubbing with other techniques, reducing chemical usage and improving efficiency. Pilot-scale systems have demonstrated the feasibility of these approaches in industrial applications, though optimization remains necessary for cost reduction.

Chemical scrubbing involves reactions such as:



This process often employs packed tower scrubbers where biogas is passed through a countercurrent flow of the chemical solution. Diagrammatically, this consists of a gas inlet, scrubbing tower with packing material, and a collection system for the scrubbed gas. For example, a $100 \text{ m}^3/\text{h}$ biogas flow treated using a sodium hydroxide scrubber can achieve H_2S removal efficiency above 99%. The addition of scrubbing systems ensures precise control over reaction conditions, optimizing the neutralization of H_2S .

1.2 Biological Desulfurization

Biological methods employ sulfur-oxidizing bacteria (e.g., *Thiobacillus* species) to convert H_2S into elemental sulfur or sulfate. This approach is cost-effective and environmentally friendly, with removal efficiencies ranging from 90% to 98% [4]. Optimization of reactor conditions, such as pH and temperature, is crucial for achieving high performance.

Research by Syed et al. [5] demonstrated the effectiveness of biotrickling filters in removing H_2S from biogas streams. Emerging studies focus on genetically engineered strains of bacteria to enhance their sulfur conversion efficiency. These approaches aim to reduce the reactor size and improve adaptability to varying biogas compositions. Combined systems integrating biological and chemical processes are also under investigation for improved reliability.

Biological methods rely on sulfur-oxidizing bacteria that facilitate reactions such as:



Technological schemes involve biofilters or biotrickling filters, with a substrate medium supporting bacterial colonies. Biogas is passed through these systems, ensuring intimate contact with the microbial population. For instance, studies demonstrate that optimized biofilters achieve up to 98% H_2S removal under steady-state conditions. Moreover, the systems are highly energy-efficient, making them suitable for long-term operation.

1.3 Activated Carbon Filtration

Activated carbon effectively adsorbs H_2S due to its high surface area and porosity. Enhanced performance can be achieved by impregnating the carbon with metal oxides. Although this method is suitable for low H_2S concentrations, its capacity diminishes rapidly at higher levels, necessitating frequent replacement [8]. Although this method is suitable for low H_2S concentrations, its capacity diminishes rapidly at higher levels, necessitating frequent replacement.

Recent developments include the use of regenerative activated carbon systems, where thermal or chemical regeneration extends the lifespan of the adsorbent. Such innovations significantly reduce operational costs and environmental impact.

These systems typically involve gas flowing through a bed of activated carbon, with provisions for regeneration or replacement. An example system treating biogas with 500 ppm H₂S showed a removal capacity of 50 mg/g activated carbon before requiring regeneration. The process can be enhanced by impregnating the activated carbon with chemicals that increase its adsorption capacity.

2.2 Methods and Studies on Carbon Dioxide Removal

Carbon dioxide (CO₂) removal enhances the methane content of biogas [10-13]. The primary methods include:

2.1 Membrane Separation

Membrane technology has emerged as a leading solution for CO₂ separation due to its compact design and low energy requirements. Gas separation membranes selectively allow CH₄ to pass through while retaining CO₂. Recent advancements in polymeric and mixed-matrix membranes have enhanced separation efficiency and durability [10].

Ongoing research focuses on the development of nanocomposite membranes, which combine high selectivity with mechanical stability. Multi-stage membrane systems are being designed to further enhance methane recovery rates while reducing operational costs.

Membrane separation operates based on selective permeability, where no direct chemical reactions occur. Gas separation membranes selectively allow CH₄ to pass through while retaining CO₂. For example, multi-stage membrane modules treating biogas with 40% CO₂ achieve methane concentrations above 96%. Membrane material properties such as selectivity and permeability play crucial roles in determining the efficiency of this process.

2.2 Pressure Swing Adsorption (PSA)

PSA utilizes adsorbent materials such as zeolites and activated carbon to separate CO₂ based on pressure changes. The process achieves high purity levels of biomethane (>97%), but its efficiency decreases with increasing CO₂ concentrations in raw biogas [11].

Innovative modifications to PSA systems include the use of advanced adsorbents with higher selectivity and improved desorption characteristics. Studies have also explored the integration of PSA with other separation methods, creating hybrid systems that optimize overall performance.

In PSA, CO₂ is adsorbed on materials like zeolites through:



The system includes adsorber columns, valves, and vacuum pumps to alternate between adsorption and desorption phases. A PSA system processing 200 m³/h biogas can yield biomethane with 99% methane purity. By carefully controlling pressure cycles, PSA ensures minimal methane losses.

2.3 Cryogenic Separation

Cryogenic methods involve cooling biogas to temperatures where CO₂ condenses and can be separated as a liquid. While this technique offers high methane recovery rates, the energy-intensive nature of cryogenic systems poses challenges for widespread adoption [12].

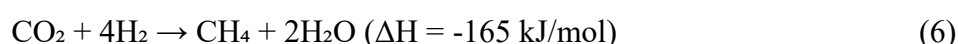
Emerging approaches aim to integrate cryogenic separation with waste heat recovery systems to improve energy efficiency. Demonstrations of such integrated systems at pilot scales indicate significant potential for reducing operational costs.

These systems use heat exchangers and expansion turbines, often coupled with waste heat recovery for improved efficiency. Cryogenic units treating biogas with 45% CO₂ have achieved methane recoveries exceeding 90%. Advanced cryogenic designs include multi-stage cooling to reduce energy consumption.

3.3 Methanation of Carbon Dioxide with Hydrogen

Methanation of CO₂ is an innovative approach that utilizes renewable hydrogen to convert CO₂ into methane through the Sabatier reaction. This process not only enhances biomethane yield but also contributes to carbon recycling [14-21].

Methanation processes involve chemical conversion of CO₂ using hydrogen (H₂) via the Sabatier reaction:



3.1 Catalytic Methanation

Catalytic methanation employs metal-based catalysts, such as nickel or ruthenium, to facilitate the reaction between CO₂ and H₂. Studies have shown that Ni catalysts offer a cost-effective solution with high conversion rates, although they are prone to deactivation due to carbon deposition [14].

Recent advancements include the development of bimetallic catalysts that enhance resistance to deactivation. Reactor designs are also being optimized to improve heat management and reaction kinetics.

Research [15] investigated the performance of Ni-based catalysts in CO₂ methanation, highlighting their efficiency and stability. Catalytic methanation utilizes reactors with nickel or ruthenium-based catalysts. These reactors are designed for efficient heat removal to prevent catalyst deactivation. Pilot systems using nickel catalysts achieve methane yields above 97% with CO₂ conversion rates exceeding 90%. The reaction's exothermic nature necessitates advanced cooling mechanisms to maintain optimal temperatures.

3.2 Biological Methanation

Biological methanation utilizes methanogenic archaea to produce methane under anaerobic conditions. This process operates at mild temperatures and pressures, making it energy-efficient. Recent research has demonstrated the feasibility of integrating biological methanation into existing biogas plants [17].

Studies are exploring co-culture systems that combine different microbial species to improve conversion efficiency. Efforts are also underway to scale up biological methanation processes for industrial applications.

In biological methanation, methanogenic archaea facilitate the above reaction under mild conditions in anaerobic digesters. For example, laboratory-scale systems integrating biological methanation with biogas plants demonstrated 95% methane yield. The natural adaptability of these microbes to variable gas compositions enhances system robustness.

In biological methanation, microorganisms such as methanogenic archaea catalyze the conversion of CO₂ and H₂ into methane under anaerobic conditions. A study [18] explored the use of mixed cultures in anaerobic reactors for efficient CO₂ reduction to methane. This process can be integrated into existing anaerobic digestion systems or operated as a separate bioreactor, offering a sustainable approach to upgrading biogas. In the article [13] reviewed various biogas

upgrading techniques and highlighted the potential of biological methanation as a sustainable method.

3.3 Plasma-Assisted Methanation

Emerging technologies such as plasma-assisted methanation show promise in enhancing reaction kinetics and reducing reliance on expensive catalysts. However, further research is needed to optimize system design and scalability [19].

The combination of plasma technology with catalytic systems is being investigated as a means to achieve higher efficiency and lower operational costs. Initial results indicate significant potential for industrial-scale deployment.

Plasma-assisted systems enhance methanation kinetics through non-thermal plasma, creating reactive species that accelerate the Sabatier reaction. These involve a plasma reactor coupled with traditional catalytic beds. Initial experiments have shown up to 85% CO₂ conversion at lower energy inputs compared to conventional methods. The versatility of plasma-assisted designs allows for integration with existing biogas plants.

Technological schemes for methanation processes typically include feed gas compressors, reactor chambers, heat exchangers, and product gas separators.

Conclusions

This review highlights the diverse methods available for biogas purification and enhancement, emphasizing their strengths and limitations. Chemical scrubbing and biological desulfurization are effective for H₂S removal, while membrane separation and PSA offer reliable solutions for CO₂ extraction. Methanation of CO₂, particularly through catalytic and biological approaches, presents a promising avenue for maximizing biomethane production and achieving carbon neutrality. Future research should focus on integrating these technologies into cost-effective and sustainable systems for large-scale applications.

Additional efforts should be directed toward hybrid systems that combine multiple purification and methanation methods to achieve synergistic benefits. Policy frameworks supporting research, development, and deployment of these technologies will be crucial in accelerating the transition to a biomethane-based energy economy.

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Pyrolysis of Waste Tires: Product Characteristics and Industrial Applications

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Abstract. The issue of waste tire accumulation and utilization is analyzed. Pyrolysis is identified as a promising recycling method, yielding gaseous, liquid, and solid products. These require further purification before use. The characteristics, processing methods, and potential applications of pyrolysis products have been briefly reviewed.

Keywords: pyrolysis oil, pyrolysis gas, waste tires, alternative fuel, pyrolysis of tires, carbon black.

Introduction

Given the depletion of global oil reserves, the search for alternative energy sources has become increasingly urgent. As light, high-quality crude oil availability declines, the oil refining industry is progressively shifting toward cheaper and heavier feedstocks. This transition drives the exploration of unconventional raw materials, including waste hydrocarbon-based materials and biomass.

Industrial waste has emerged as one of the most critical environmental challenges, threatening ecological stability. The growing volumes of industrial and municipal waste pose a substantial risk to society and natural ecosystems. Consequently, the rational utilization of industrial waste has become a highly relevant issue that demands prompt and effective solutions due to its profound impact on environmental quality and public health.

Notably, reusing industrial waste – such as used tires, waste oils, and plastics – for producing energy resources offers a viable strategy for mitigating environmental harm [1, 2].

Among the various categories of waste contributing to environmental pollution, used (waste) tires (WAT) occupy a particularly critical position, posing a significant threat to ecosystem diversity and human health. Their substantial volume and disposal complexity renders them a key environmental concern.

Tires are essential consumables in operating all types of motor vehicles. According to the European Tyre & Rubber Manufacturers Association (ETRMA), approximately 289 million tires are sold annually within the European Union, accounting for only 20% of the global tire market, totaling around 1.5 billion units annually [1]. According to Eurostat data, the average number of passenger vehicles in the EU is 560 per 1,000 inhabitants [1]. In Ukraine, used car tires are classified as hazardous waste (Class IV) under the Law of Ukraine “On Waste” and require specialized disposal at certified facilities [1]. As of 2020, Ukraine had approximately 245 passenger cars per 1,000 inhabitants – excluding freight and specialized vehicles – which is steadily increasing [1]. Figure 1 presents comparative data on WAT generation across various countries as of 2021 [1].

Waste tires are non-biodegradable and, due to their complex thermomechanical structure, are difficult to reuse or recycle without prior mechanical or thermal treatment [2]. The continuous accumulation of used tires presents a serious environmental and public health hazard. Improper

disposal, including illegal dumping and accumulation, increases the risk of uncontrolled combustion, which releases toxic pollutants into the environment [1, 2]. Consequently, millions of WATs are required to be appropriately disposed of each year. However, Ukraine lacks a centralized system for WAT collection. Disposal and recycling operations are carried out only by a few private enterprises operating in select regions [2].

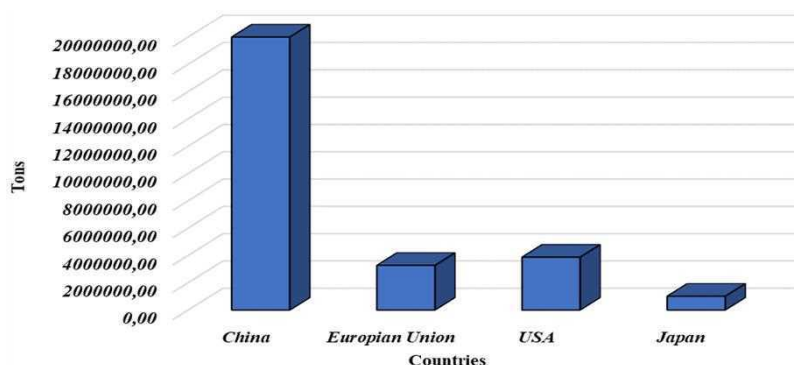


Fig. 1. The annual production of WAT in some countries.

Automobile tires are complex engineering products characterized by a multi-component structure and composition. A typical tire contains more than 200 individual substances. The primary constituents used in tire manufacturing include natural and synthetic rubber, carbon black, inert fillers (such as amorphous precipitated silica and alumina), steel, textile and fabric reinforcements (e.g., nylon, Kevlar), sulfur, zinc oxide, as well as various antioxidants and antiozonants [1].

Figure 2 illustrates the average qualitative composition of automobile tires, which varies depending on the vehicle type (passenger cars, trucks, buses, aircraft, etc.) and regional climatic conditions. Figure 3 provides a schematic representation of a passenger car tire, highlighting the key structural components that comprise the tire.

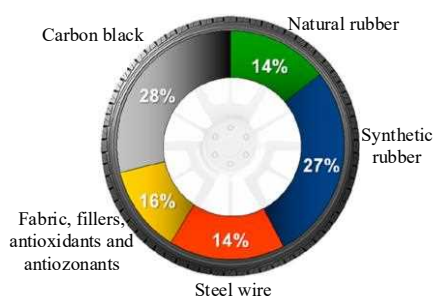


Fig. 2. Average composition of a passenger tire by weight.

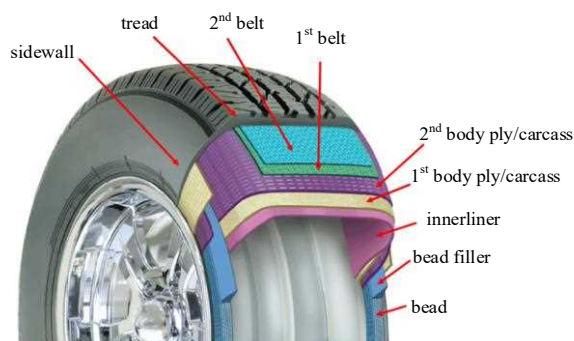


Fig. 3. Exploded view of a commercial passenger car tire.

To fulfill their primary function and ensure long service life, tires are manufactured using materials resistant to biodegradation [1, 2]. The predominant component is rubber (approximately 45 – 47%), owing to its excellent elasticity and damping properties [1, 2]. Rubber compounds typically consist of blends of natural rubber (e.g., polyisoprene) and synthetic rubbers such as polybutadiene, styrene-butadiene rubber (SBR), and (halo)butyl rubber. The specific ratios of these rubbers vary depending on the intended application of the tire.

As illustrated in Figure 3, rubber materials are primarily concentrated in the tread (approximately 32.5 wt%) and sidewalls (about 22 wt%) [1, 2]. To enhance mechanical strength and wear resistance, reinforcing agents such as carbon black and silica (around 21 – 22.5% of

tire mass) are added to the rubber compound [1, 2]. Carbon black is crucial in improving abrasion resistance and dissipating heat from the tread area, thereby preventing thermal degradation.

Steel components are incorporated to reinforce the tire structure and provide mechanical strength and durability [1, 2]. Sulfur is used as a vulcanizing agent, which improves the rubber matrix's elasticity, hardness, and structural integrity [1, 2], while zinc oxide acts as an activator, accelerating the vulcanization process [1, 2]. It is important to note that these components' exact composition and proportions may vary depending on performance requirements and tire design specifications.

The outer layer of the tire, responsible for traction through contact with the road surface, is known as the tread. It comprises a specific rubber compound and a patterned design to ensure optimal grip with minimal wear [1, 2]. Structurally, the tread is divided into three main zones: the cap (the uppermost layer in direct contact with the road), the base (located beneath the cap, designed to reduce rolling resistance), and the shoulder area (situated at the outer edges, forming a transitional zone between the tread and the sidewall).

To enhance stability, the tread is typically reinforced with two steel belts of steel cords arranged at opposing angles. Beneath the belts lies the carcass or carcass layer, which serves as the main structural framework of the tire. It usually comprises one or two plies made from polyester, rayon, or nylon cords embedded in rubber.

The inner liner on the inside of the tire comprises a thin layer of synthetic rubber, most commonly halogenated polyisobutylene, designed to provide air impermeability and maintain internal pressure. The bead, formed by steel wires encased in a rubber matrix (bead filler), ensures an airtight and secure connection between the tire and the wheel rim [1, 2].

Due to this complex, multilayered composition, tires cannot be directly reused once they end their service life. The heterogeneity of materials complicates selecting a practical and environmentally sound disposal or recycling method.

The primary waste automobile tires (WAT) disposal and recycling methods include landfilling, material reuse, incineration, pyrolysis, carbon black recovery, and their application in civil engineering projects [1, 2]. Additionally, a portion of WAT is utilized to produce modified bitumens, contributing to improving road construction materials [1, 2].

Due to their high calorific value, WATs are also considered a valuable energy resource, which has led to their reuse in various industrial sectors. Thermochemical processes such as pyrolysis [1, 2], gasification [1, 2], and combustion [1, 2] enable the efficient recovery of energy and valuable secondary products.

The methods of disposal of WAT and their common areas of application are presented in Fig. 4. Secondary products, while simultaneously reducing reliance on conventional fossil fuels.

As can be seen from Fig. 4, the methods of WAT disposal can be divided into five groups [1, 2]:

- shredding into rubber crumb and using as a component of road coverings;
- recycling – restoration of the operational characteristics of car tires by physicochemical methods for a specific time;
- thermal methods – incineration (the simplest but the most non-ecological method), gasification (for the production of gases), and pyrolysis (one of the most promising methods);
- use as a building material;
- storage in landfills or on specialized sites.

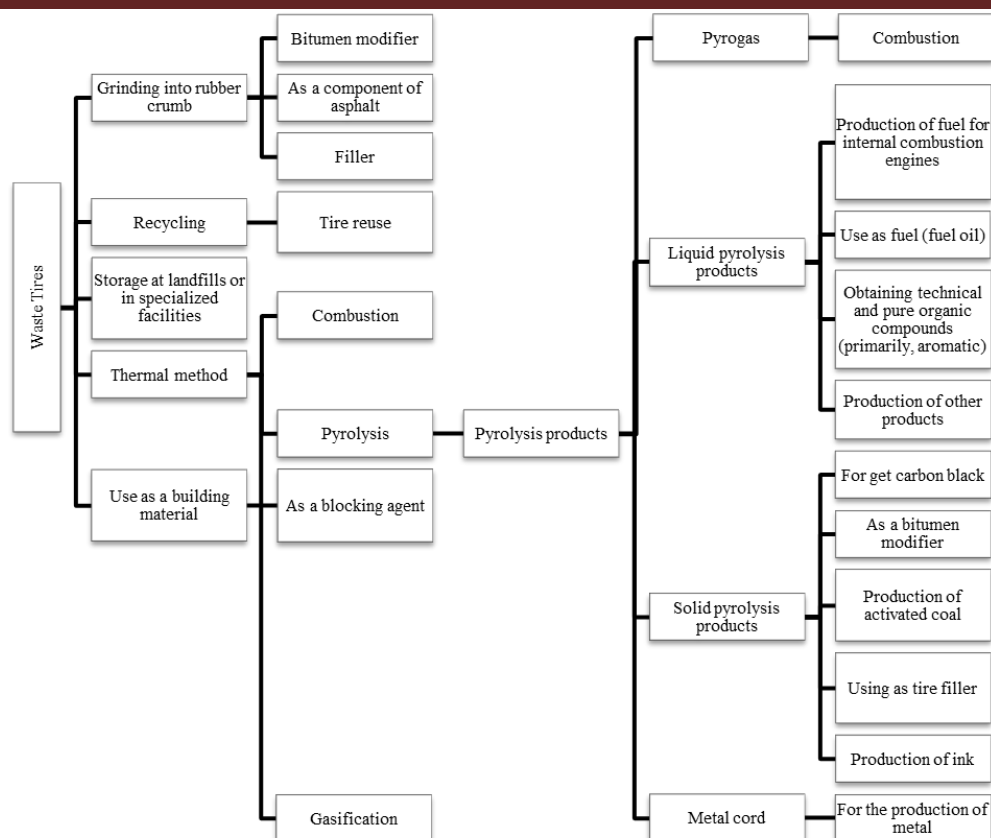


Fig. 4. Methods of disposal of WAT and their common application areas.

In light of the significant volume of waste automobile tires (WAT) generated globally, they represent a valuable secondary raw material for producing a wide range of products and new energy resources. However, due to their complex structure and composition, selecting an appropriate method for rational utilization presents a challenge. Among the various WAT disposal methods that yield diverse products, pyrolysis is an auspicious process enabling producing fuel and chemical raw materials. The following is a brief review of the pyrolysis process of used tires and an overview of the characteristics and potential applications of the products obtained through this method.

Conclusions

Considering the significant volume of global waste automobile tires (WAT) generated, their proper disposal and recycling present a critical ecological and economic challenge. Pyrolysis of waste tires emerges as one of the most promising methods for their utilization, as it allows for producing energy resources and chemical raw materials, which can be applied in various industries. However, the complex structure of WAT requires the selection of efficient technologies to ensure their effective processing and minimize environmental impact.

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Investigation of the Energy Characteristics of Sunflower Stalks and Their Separated Tissues as Lignocellulosic Raw Materials for Solid Biofuel Production

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Abstract. *The purpose of this research was to investigate the energy characteristics of sunflower stalks and their separated tissues, which differ in chemical composition. Due to their adequate calorific value but excessive ash content, the rind and whole sunflower stalks were recommended as components of solid composite fuel.*

Keywords: sunflower, rind, pith, filtration drying method, differential thermal analysis (DTA), calorific value, ash content.

Introduction

The search for new alternative energy sources remains a pressing global priority. Among various types of biomass, agricultural residues hold significant potential as a source of lignocellulosic material for solid fuel production due to their rapid renewability, environmental sustainability, and high calorific value. Furthermore, utilizing agricultural waste for energy production also helps address the issue of waste disposal in the agricultural sector.

Sunflower (*Helianthus annuus* L.) is a rapidly growing, high-yielding crop primarily cultivated for its seeds and oil. Currently, global sunflower seed production reaches 56.7 million metric tons (MMT), and sunflower cultivation covers over 27 million hectares worldwide [1, 2]. Additionally, the substantial above-ground biomass yield of 45–75 tons per hectare leads to considerable post-harvest residue accumulation [3, 4]. However, a large proportion of sunflower stalks is not managed sustainably.

Sunflower stalks, with considerable height (0.6–2.5 m) and stem diameter (2–7 cm), possess a complex, multi-layered anatomical structure unique to this crop. The inner part of the stalk is filled with spongy, thin-walled, large-celled parenchyma tissue known as pith. Thus, the idea emerged to separate sunflower stalks into individual components – the pith and outer tissues (rind) – and to investigate their fuel characteristics separately, comparing them with those of whole stalks.

This study aims to investigate the energy characteristics of sunflower stalk pith and rind as individual tissues, as well as of whole stalks, as potential raw materials for solid fuel production.

Results and Discussion

Sunflower (*Helianthus annuus* L.) stalks were collected after the seed harvesting period. The stalks were cut lengthwise to separate the pith from the outer rind tissues. To prepare sunflower stalk rind (SSR), sunflower stalk pith (SSP), and sunflower stalk general (SSG) test samples, the rind, pith, and entire stalks were ground separately in a jaw crusher to a particle size of 0.01–5 mm.

The average contents of lignin, cellulose, and hemicellulose in the SSR, SSP, and SSG samples are presented in Table 1. Notably, the composition of the SSP sample differs

significantly from that of the other stalk samples, as it contains lower levels of hemicellulose and lignin but a high pectin content (approximately 23.2% [5]).

Table 1

Composition of sunflower stalk samples, along with their calorific values and ash content

Samples	Cellulose, wt.% d.m.	Hemicellulose, wt.% d.m.	Lignin, wt.% d.m.	Calorific values, MJ/kg d.m.	Ash content, wt.% d.m.
SSR	39.4	28.5	19.8	18.2	8.8
SSP	34.2	6.3	3.8	7.4	16.1
SSG	35.3	20.4	15.8	14.2	10.2

To reduce the moisture content of the SSR, SSP, and SSG samples, a filtration drying method was applied as an energy-efficient approach [6, 7]. Drying kinetic curves for the sunflower stalk samples are presented in Fig. 1.

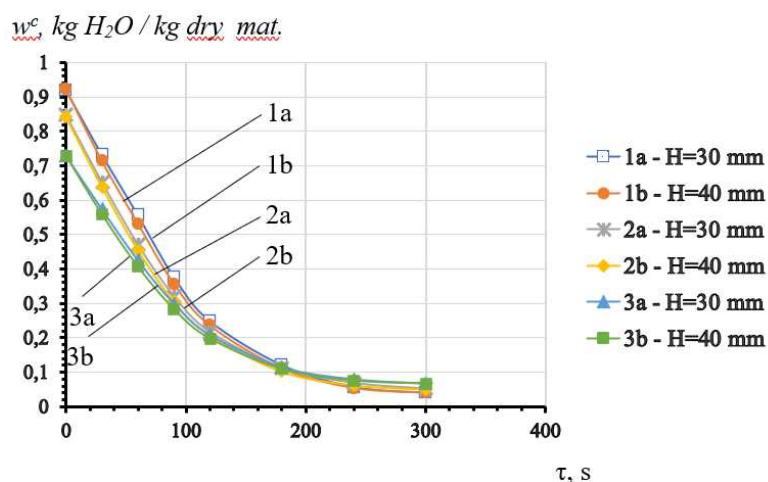


Fig.1. Drying kinetic curves for sunflower stalk samples: 1a, 1b – SSR; 2a, 2b – SSG; 3a, 3b – SSP.

To examine the dried SSR, SSP, and SSG samples under high-temperature conditions, differential thermal analysis (DTA) was conducted using a Q-1500 derivatograph of the Paulik–Paulik–Erdey system. To predict the calorific values of the samples, a comparison of the DTA curves is shown in Fig. 2.

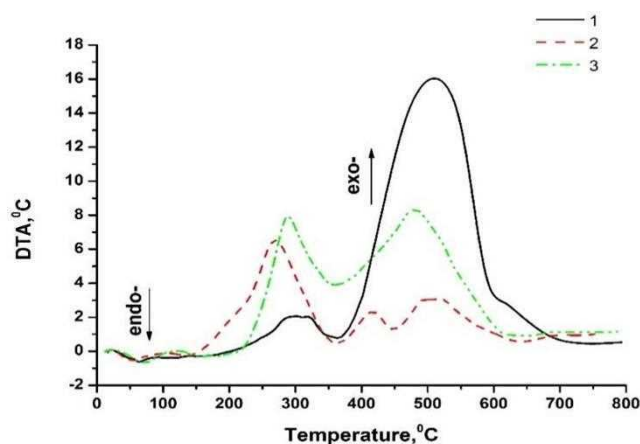


Fig. 2. DTA curves of sunflower stalk samples: 1 – SSR; 2 – SSP; 3 – SSG.

As shown by the DTA curves, the SSR sample exhibited the highest calorific value, with combustion of its pyrolytic residue in the temperature range of 377–750°C accompanied by the

most pronounced exothermic effect. The SSP sample had the lowest calorific value, as evidenced by the presence of only minor exothermic effects during combustion of its pyrolytic residue at 360–750°C. The calorific value of the SSG sample was lower than that of the SSR sample but higher than that of the SSP sample.

Additionally, the calorific values of the SSR, SSP, and SSG samples were determined using a precision bomb calorimeter B-08-MA, and the results are shown in Table 1. The calorific values of the SSR and SSG samples were consistent with data for herbaceous and agricultural biomass, which typically show calorific values of approximately 14–18 MJ/kg dry matter.

To determine the ash content, 1 g of each sample was carbonized in an oven at 550°C for 3 hours. The SSP sample exhibited the highest ash content (Table 1) due to its high concentration of inorganic substances.

The chemical composition of the ash obtained after combustion of the SSR sample (SSR ash) was determined through X-ray fluorescence (XRF) analysis and is presented in Table 2. Similar information for the ash of the SSP sample is presented in Table 3.

Table 2

Chemical composition of the ash obtained after the combustion of the SSR sample and XRF spectras

Chemical composition of the SSR ash, wt. %		XRF spectras of SSR ash sample	
		Light elements	Heavy elements
MgO	6.1±0.1		
SiO ₂	4.1±0.04		
P ₂ O ₅	3.8±0.02		
SO ₃	2.2±0.01		
K ₂ O	38.0±0.1		
CaO	44.5±0.3		
Fe ₂ O ₃	0.5±0.01		
Other oxides	0.8±0.01		

Table 3

Chemical composition of the ash obtained after the combustion of the SSP sample and XRF spectras

Chemical composition of the SSP ash, wt. %		XRF spectra of SSP ash sample	
		Light elements	Heavy elements
MgO	2.7±0.1		
SiO ₂	0.4±0.02		
P ₂ O ₅	0.2±0.01		
SO ₃	0.5±0.01		
K ₂ O	28.6±0.08		
CaO	67.2±0.1		
Fe ₂ O ₃	0.2±0.01		
Other oxides	0.2±0.01		

The chemical compositions of the SSR and SSP ash samples differed slightly as shown by X-ray fluorescence (XRF) analysis.

Conclusions

To reduce the moisture content of the sunflower stalk samples (SSR, SSP, and SSG), a filtration drying method was applied as an energy-efficient approach, and the dried materials were subsequently used for further research. In general, the calorific values of the sunflower stalk samples were found to be directly influenced by their chemical composition, particularly the relative contents of cellulose, hemicellulose, and lignin. The calorific values determined using a bomb calorimeter were 18.2 MJ/kg for the SSR sample, 14.2 MJ/kg for the SSG sample, and 7.4 MJ/kg for the SSP sample. The calorific values of the SSR and SSG samples were consistent with data for herbaceous and agricultural biomass, which typically show calorific values of approximately 14–18 MJ/kg dry matter. The highest lignin content in the SSR sample resulted in its highest calorific value, whereas the low lignin content in the SSP sample led to its lowest calorific value. Additionally, the presence of inorganic compounds played a crucial role in ash formation. The experimentally determined ash contents were 8.8 wt.% for SSR, 10.2 wt.% for SSG, and 16.1 wt.% for SSP. The SSP sample showed the highest ash content caused by the highest content of inorganic substances. The chemical compositions of the SSR and SSP ash samples differed slightly, as shown by X-ray fluorescence (XRF) analysis. Given their favorable calorific values but relatively high ash contents, sunflower stalk rind and whole sunflower stalks are recommended as potential components of solid composite fuel based on woody biomass. Conversely, due to its low calorific value and high ash content, sunflower stalk pith is not considered a viable option for solid biofuel production as a standalone material.

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The Influence of Dehydration Mode on the Duration of the Drying Process of Protein-Containing Raw Materials of Animal Origin

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Abstract. *The kinetics of drying of protein-containing raw materials of animal origin were studied, and the most rational modes of drying pork meat using the combined infrared-convective method of 100W + 55 °C and the form (cubes, granules) were established. The recovery properties of dried meat were determined depending on the dehydration modes and the shape of the samples.*

Keywords: drying, combined dehydration methods, recoverability, protein-containing raw materials of animal origin, pork meat.

Introduction

The production of meat products is acquiring new forms of consumption, which is associated with the development of human life and the development of modern meat processing technologies. The modern range of dry meat products includes meat flakes, chips, sticks, jerkies, charkas, biltong, pemmican, pastirma, nikki, yukola, and others [1, 2, 3, 4]. At the same time, the fast food industry, which includes dried meat, is developing. The main requirements are the safety and naturalness of such a product.

Meat drying has been used for a long time to preserve this product for a long time. It was used in ancient Egypt, Spain, and Mexico. And in ancient literature, Plato, Euripides and Homer described feasts with a wide variety of meat products. On the tables of ancient Greek and Roman rulers and nobles, salted, dried, smoked, and cured meat of domestic and wild animals was present in huge quantities [5].

Meat is an essential source of protein, which builds human muscle tissue. It is especially necessary for people engaged in heavy physical labour, as well as for military personnel, athletes, travellers, and tourists. Dried meat retains proteins, trace elements, and amino acids in a more concentrated form and contains zinc, iron, and B vitamins, which are beneficial for human health.

Dried meat - when eaten, it gradually swells in the stomach, slowly saturating the body with useful food components, giving a feeling of satiety and a surge of energy. It's a simple snack that helps you quickly regain your strength. Which is very important for people who are subjected to intense physical activity [5].

Drying processes consume 27% of the energy produced in Ukraine. This means that drying processes are energy-intensive. Therefore, the challenge is to dry protein-containing raw materials of animal origin while reducing process costs and maintaining product quality.

In recent years, various variants of drying plants using microwave energy have been proposed, including in various combinations with other methods: convection, infrared radiation, ultrafiltration, etc. [6].

However, there are no such installations of domestic production [5]. Drying is a modern method of processing raw meat. The advantage of this method is that the process is carried out without the use of preservatives or flavour enhancers, such as monosodium glutamate, sodium nitrite, food colours, flavours, anti-caking agents, etc.

Therefore, the main task was to study the kinetics of dehydration and establish effective drying regimes for pork meat in order to reduce energy consumption, to investigate the effect of sample shape, and the recovery properties of the dried product under different dehydration regimes.

Results and discussion

The drying study was carried out on a convective stand with automatic data collection and processing, with a block of infrared lamps installed in the drying chamber, with the ability to adjust the heat flux from 100 W/m^2 to 3800 W/m^2 .

The power of the lamps is controlled by a rheostat-type regulator [7]. Preliminary preparation of raw materials for drying includes cooking for 20 minutes and grinding into cubes and pellets with a weight of 0.5 g in both cases.

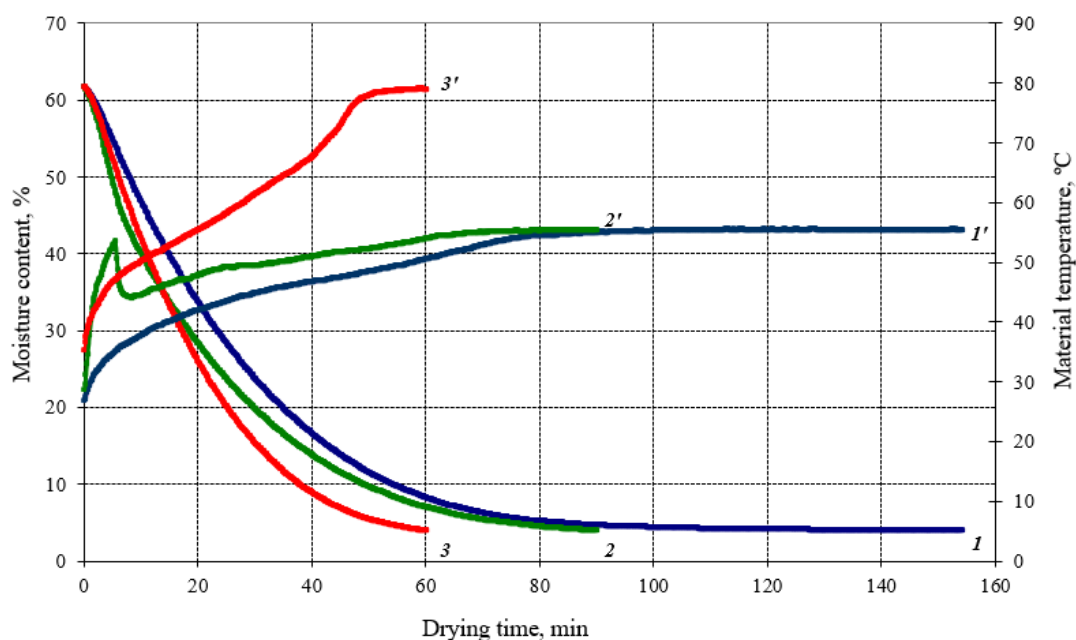


Fig. 1. Influence of heat carrier temperature on the drying time of pork meat (granules $d=5 \text{ mm}$, weight 0.5 g)

$v = 3 \text{ m/s}$, $d = 10 \text{ g/kg dry air}$:

1,1' - 55°C ; 2,2' - $3800 \text{ W/m}^2 + 55^\circ\text{C}$; 3,3' - 80°C .

Fig. 1 shows the effect of the heat carrier temperature on the duration of drying pork meat in the form of granules under convective dehydration modes of 55°C , 80°C , and the combined method of $3800 \text{ W/m}^2 + 55^\circ\text{C}$. The essence of the combined method is the simultaneous supply of energy from two energy sources (convective and infrared radiation (IR)).

As can be seen from Fig. 1, the duration of drying pork meat in the form of granules at a heat carrier temperature of 55°C (curves 1, 1') is about 157 min, and at 80°C (curves 3, 3'), the process is 2.6 times shorter, which is logical.

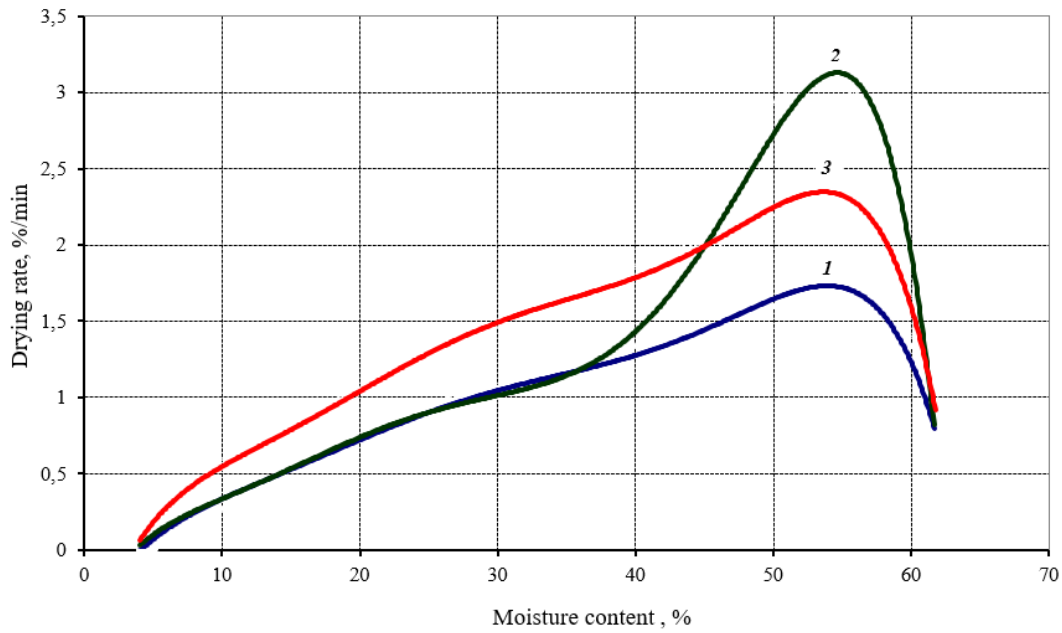


Fig. 2. Influence of heat carrier temperature on the drying rate of pork meat
(granules $d=5$ mm, weight 0,5 g)
 $v = 3$ m/s, $d = 10$ g/kg dry air:
1 – 55°C ; 2 – $3800\text{ W/m}^2 + 55^{\circ}\text{C}$; 3 – 80°C .

Curves 2, 2' show the mode of combined drying, wherein at the beginning of the process, two types of energy carriers (convective and IR) were used until the sample temperature reached 53°C , then the IR energy carrier was switched off, and drying continued with the convection method. As a result, the temperature of the material dropped sharply to 45°C , and then the heating occurred gradually. The drying time in the combined mode is 1.7 times faster compared to the mode, and the drying rate is the highest at 3.1 %/min, as can be seen from Fig. 2.

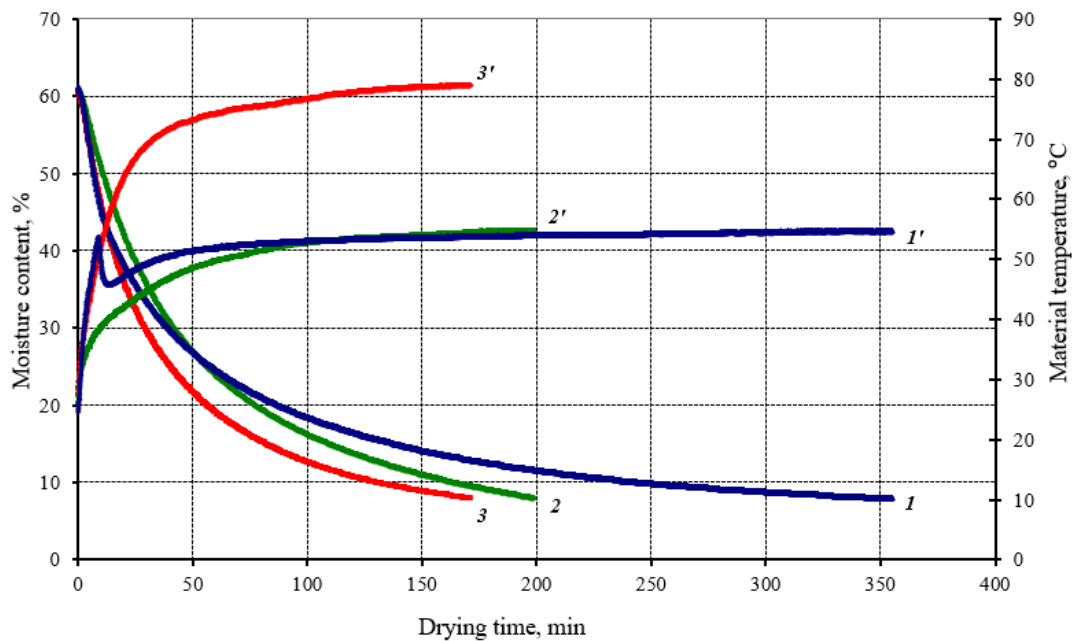


Fig. 3. Influence of heat carrier temperature on the drying time of pork meat
(cubes $d=5$ mm, weight 0,5 g), $v = 3$ m/s, $d = 10$ g/kg dry air:
1,1' - 55°C ; 2,2' – $3800\text{ W/m}^2 + 55^{\circ}\text{C}$; 3,3' – 80°C .

Similarly, the drying of pork meat under the same dehydration regimes in the form of cubes was investigated. The drying curves of the samples (Fig. 3) have a similar process character to the curves of the samples in the form of granules (Fig. 2). As shown in Fig. 3, the duration of drying the cubes at a heat carrier temperature of 55 °C is 357 min, which is 2.1 times longer than at a coolant temperature of 80 °C.

In the combined mode, the process duration is 200 min, and the process is 1.8 times faster (Fig. 3). The drying rate of pork meat samples in the form of cubes is the highest with the combined drying method and is 2.05 %/min (Fig. 4).

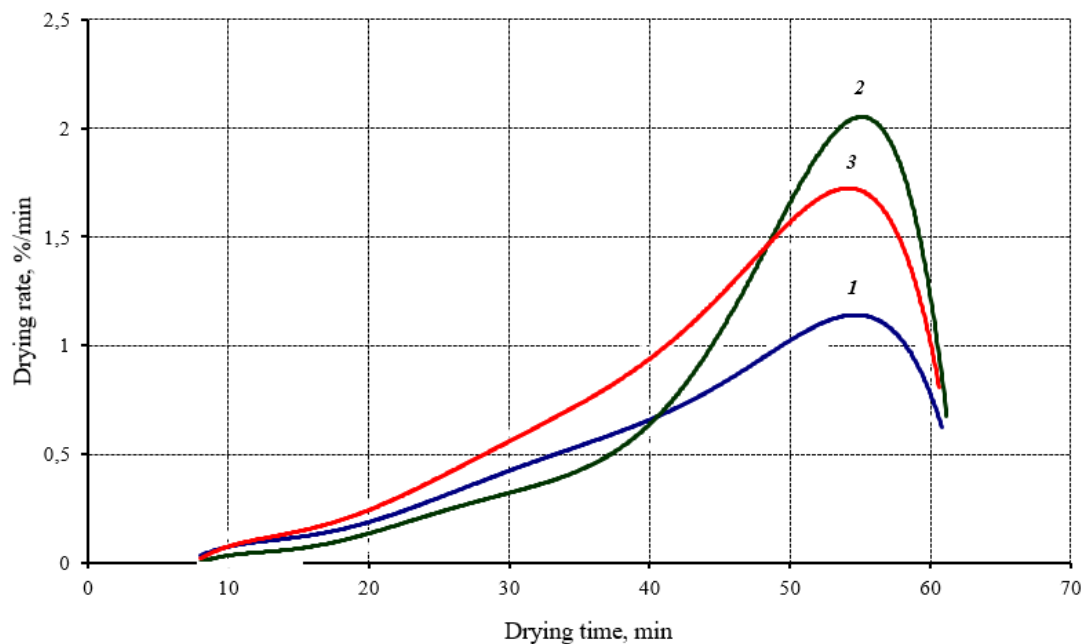


Fig. 4. Influence of heat carrier temperature on the drying rate of pork meat (cubes $d=5$ mm, weight 0,5 g), $v = 3$ m/s, $d = 10$ g/kg dry air:
1,1' - 55°C; 2,2' - 3800 W/m² + 55 °C; 3,3' - 80 °C.

Comparing the data of Figures 1 - 4, we observe that drying of protein-containing raw materials of animal origin in order to reduce energy consumption is advisable to dry in the form of granules, since the duration of drying of cubes in the effective combined mode is 200 minutes, which is 2.2 times longer. Drying time in the form of granules is 90 minutes.

Swelling is assessed using the swelling coefficient (C_{swell}), which shows the relative increase in product weight after swelling and determines the ability to restore the original qualities of the material when dehydrated [5].

The swelling coefficient is determined by the formula:

$$C_{swell} = \frac{G_2}{G_1}, \quad (1)$$

where C_{swell} – swelling coefficient;

G_1 and G_2 – are the masses of the material before and after swelling, respectively, g.

Material recoverability R is a value that shows how close the moisture content of the recovered material is to the original mass, which is assumed to be 100%. It is determined by the formula:

$$R = \frac{S_0}{S_1} * C_{swell} * 100 \%, \quad (2)$$

where S_0 - dry matter content in the initial material, %, $S_0 = 100 \% - W_{init}$

S_1 - dry matter content in dried material, %, $S_1 = 100 \% - W_{final}$



Fig. 5. Photo of the test sample (pork meat) after drying in the form of granules.



Fig. 6. Photo of the test sample (pork meat) after drying in the form of cubes.

Figures 5 and 6 present photographs of the studied pork meat samples after drying in the form of granules and cubes. Figs. 7 and 8 present the results of experimental studies to determine qualitative indicators, namely the swelling coefficient and recoverability of the studied samples after drying according to the standard method [5].

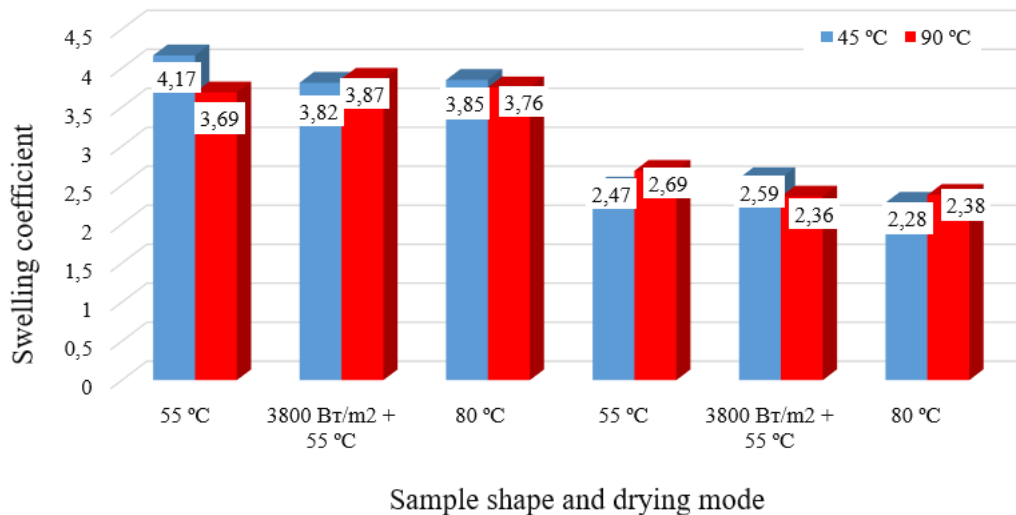


Fig. 7. Swelling coefficient of pork meat at holding temperatures of 45 °C and 90 °C.

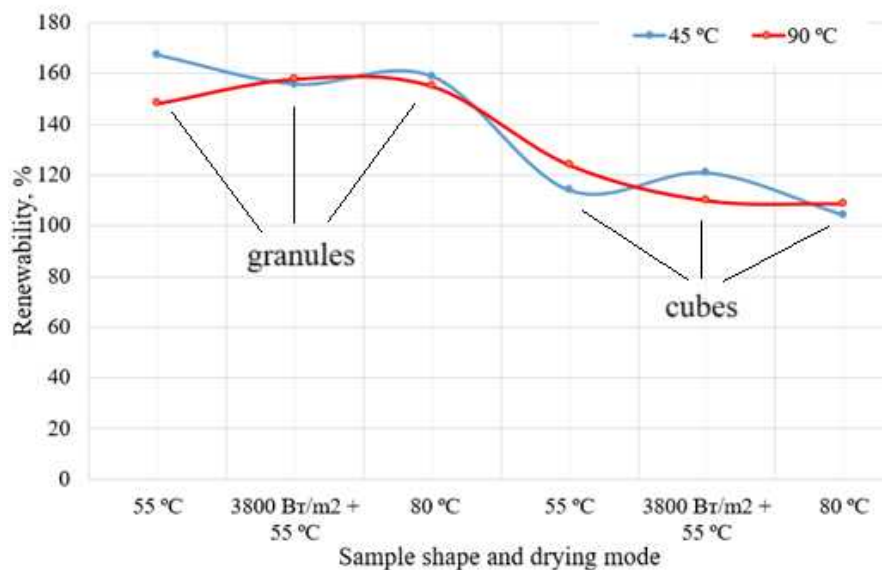


Fig. 8. Recoverability of pork meat at holding temperatures of 45 °C and 90 °C.

The qualitative indicators of the samples were determined at holding temperatures of 45 °C and 90 °C for both granules and cubes. Figure 7 shows that the swelling coefficient of pork meat in the form of granules is higher compared to that in the form of cubes for all studied drying modes, in particular for the combined mode $3800 \text{ W/m}^2 + 55 \text{ °C}$ the indicator for granules is 3.82 and 3.87 at 45 °C and 90 °C, respectively, and for cubes - 2.59 and 2.36 at 45 °C and 90 °C, respectively.

Fig. 8 shows the results of studies on the recoverability of protein-containing raw materials of animal origin at holding temperatures of 45 °C and 90 °C. Similarly, samples in the form of granules have higher recoverability compared to samples in the form of cubes.

Conclusions

As a result of experimental studies, it was found that it is advisable to carry out dehydration of protein-containing raw materials of animal origin at an effective mode of $3800 \text{ W/m}^2 + 55 \text{ °C}$ in the form of granules, since in this case the drying time is 3.9 times faster than in the case of a sample in the form of cubes. This dry product can be used in fast food products.

Determination of qualitative characteristics (swelling and recovery coefficient) made it possible to determine that samples in the form of granules have a greater ability to swell and recover the dry product.

Therefore, the use of pork meat in instant products is more rational if it is chopped and dehydrated in the form of granules.

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The Influence of Polyethylene on the Thermophysical Properties of Fuel from Municipal Solid Waste

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Abstract. Thermal analysis was carried out, and the heat of combustion of the experimental fuel was determined in order to study the influence of polyethylene on the properties of fuel from municipal solid waste. It is shown that fuel samples with a high polyethylene content have high values of net calorific value and intense gas formation.

Keywords: municipal solid waste, polyethylene, fuel, thermal analysis, calorific value.

Introduction

The technology of waste combustion in cogeneration plants with the production of electrical and thermal energy is the most common and one of the most effective among technologies for the energy use of municipal solid waste (MSW). In addition, technologies for processing MSW into fuel are actively developing in the world. Simultaneously with the involvement of solid waste in the energy sector, environmental problems associated with the disposal of waste in landfills and dumps will be solved, which leads to catastrophic pollution of air, soil, surface, and groundwater.

Fuel from waste is obtained according to the requirements of the end consumer. Technologies for processing MSW into refuse derived fuel (RDF) or solid recovered fuel (SRF) depend on the characteristics of the raw material. The processing of MSW into fuel involves the sorting of waste and the separation of combustible components. Paper, cardboard, plastic and textiles have the largest share of combustible components of MSW [1, 2].

Plastic is one of the main components of MSW. It needs to be handled properly as a fuel to reduce its negative impact on the environment. There are various chemical forms of plastic waste (polyethylene PE, polypropylene PP, polyvinyl chloride PVC, polyamide PA, polystyrene PS, polyethylene terephthalate PET, etc.) with different physical and chemical properties and composition [3]. It should be noted that PE and PP are suitable for combustion as part of a composite fuel [3]. At the same time, PE has the highest calorific value (44.8 MJ/kg) [4]. Therefore, it is important to analyze variations in the composition of fuel with different PE content in order to obtain fuel from MSW with high-quality characteristics.

Materials and methods

The thermal characteristics of the combustible components of MSW were previously determined with the aim of creating an alternative composite fuel [5]. It was found that most components, except polyethylene, can be classified as lignocellulosic biomass based on their elemental composition and the nature of thermal decomposition.

The main characteristics of MSW-based fuel are determined during its combustion. The combustion behavior of fuel can be predicted based on the results of thermal analysis. Samples of experimental RDF were made taking into account the morphological composition of MSW in

Ukraine [6] and with the aim of studying the influence of polyethylene as a component with the highest calorific value (Table 1). The studies were carried out by the method of thermal analysis in a Q-1000 derivatograph in static conditions of a gas environment. The fuel samples were heated at a constant rate from ambient temperature to 1000 °C. Data on the change in temperature and mass of the sample (TG), the rate of change in mass (DTG), and the heat release (DTA) were obtained during heating (Figs. 1 and 2).

Table 1

The RDF composition

Sample	Fuel components, %				
	polyethylene	cardboard	fabric	genuine leather	pine wood
RDF 1	26	50	16	3.5	4.5
RDF 2	31	29	13	4	23
RDF 3	40	37	15	3.5	4.5
RDF 4	50	50	-	-	-
RDF 5	50	-	20	10	20

Results

Processing of experimental data made it possible to determine the temperature ranges of dehydration, thermal decomposition, moisture and ash content, as well as the content of decomposable organic and mineral substances (Table 2).

Table 2

Thermal characteristics of experimental fuel

Sample	Water removal		Thermal decomposition				Ash, % dry matter	Net calorific value, MJ/kg
			organic substances		mineral substances			
	range, °C	moisture content, %	range, °C	content, % dry matter	range, °C	content, % dry matter		
RDF 1	23–166	6.28	166–530	91.32	530–1000	3.81	4.87	23.03
RDF 2	20–165	5.17	165–534	92.79	534–1000	3.69	3.52	25.22
RDF 3	23–166	4.69	166–538	92.69	538–1000	3.58	3.73	27.01
RDF 4	23–157	3.81	157–534	90.54	534–1000	4.73	4.73	28.89
RDF 5	23–154	4.51	154–544	95.92	544–1000	2.19	1.89	30.82

Sample RDF 1 has the lowest polyethylene content in its composition. Fuel dehydration occurs in the range of 23–166 °C (Fig. 1 and 2, TG, DTG, and DTA curves). The moisture content of the sample is the highest among the fuels due to the high cardboard content (Table 2). Thermal decomposition of organic substances occurs in three stages, differing in decomposition rate and thermal effects (Fig. 2, DTG and DTA curves). At the first stage (166–352 °C), a constant increase in heat release is observed; the maximum decomposition rate is recorded at a temperature of 313 °C (Fig. 2, DTG curve). At the second stage (352–470 °C), the intensity of decomposition increases. The release of gases outside the decomposition zone results in heat loss. This is recorded on the DTA curve as an endothermic peak with a maximum at 463 °C. The decomposition of organic matter is completed at the third stage in the range of 470–530 °C. This is evidenced by the course of the DTG and DTA curves. A further increase in temperature causes the decomposition of mineral substances. At temperatures of 648–733 °C, a loss of sample mass (Fig. 1 and 2, TG and DTG curves) and heat absorption are recorded, which is a consequence of

the thermal dissociation of calcium carbonate present in the cardboard. RDF 1 has the highest ash content and the lowest calorific value (Table 2).

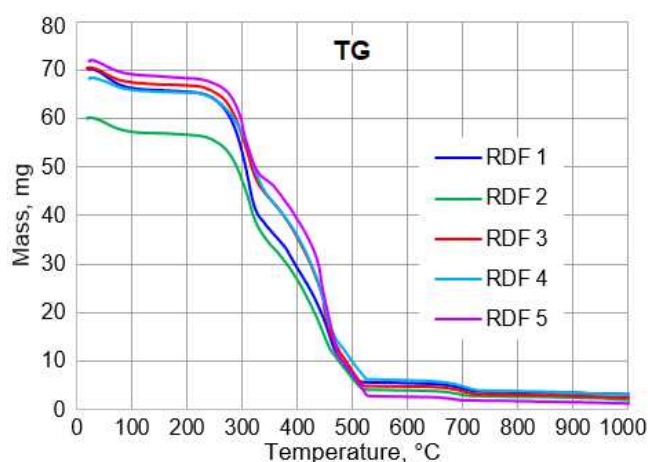


Fig. 1. Combined TG curves.

Increasing the polyethylene content in RDF 2 to 31% does not cause significant differences in the nature of thermal decomposition (Figs. 1 and 2). Dehydration occurs when reaching 165 °C. After this, the decomposition of organic substances occurs in three stages. Heat generation increases in the second stage and reaches its maximum at 481 °C. Thermally unstable mineral substances of fuel components decompose in the range of 534–1000 °C. The process of decomposition of calcium carbonate was observed in the range of 643–725 °C. Increasing the polyethylene content causes an increase in the calorific value to 25.22 MJ/kg.

Dehydration of RDF 3, containing 40% polyethylene, ends at 166 °C. After which, decomposition of organic substances begins (Figs. 1 and 2). It is also characterized by three stages. The intensity of decomposition increases due to the high polyethylene content in the fuel. An increase in the polyethylene content causes changes in the nature of the destruction of organic substances. A strong endothermic peak is recorded on the DTA curve in the range of 419–501 °C (Fig. 2). The impact of polyethylene as a fuel component becomes more noticeable and causes a powerful emission of environmentally hazardous [7] decomposition products. At the same time, the calorific value of RDF 3 increases due to the contribution of the calorific value of polyethylene (Table 2).

RDF 4, containing cardboard and polyethylene in equal proportions, is characterized by low moisture content (Table 2). The destruction of organic substances occurs in accordance with the patterns characteristic of the RDF 3 sample. The calorific value of the fuel is 28.89 MJ/kg.

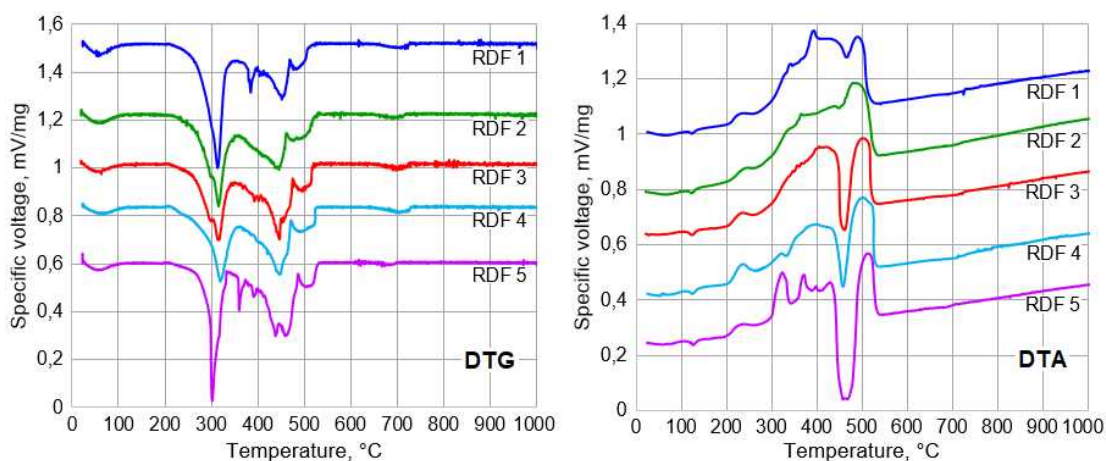


Fig. 2. Combined DTG and DTA curves.

The RDF 5 differs by the absence of cardboard in its composition and a high content of polyethylene (Table 1). Thermal decomposition of organic substances is accompanied by intense gas formation. RDF 5 has a low content of thermally unstable mineral substance and ash, as well as the highest calorific value of 30.82 MJ/kg.

Studies have shown that all fuel samples have a similar nature of thermal destruction, since the main components of the fuel are polyethylene and lignocellulosic raw materials. It can be noted that the high content of polyethylene in RDF determines not only the high calorific value of the fuel, but also the powerful release of volatile products of thermal decomposition, which improves combustion kinetics. It would be rational to have the maximum amount of polyethylene in the fuel based on the calorific value and kinetics of thermal decomposition of experimental RDF. However, in practice, the polyethylene content in the fuel will be determined by the emission purification system of a particular energy company.

Conclusions

Based on the data obtained, the presented RDF compositions can be recommended, since they satisfy the conditions put forward for the fuel. However, it is necessary to ensure the neutralization of harmful substances formed during the thermal decomposition of polymeric materials when burning such fuel. The results show that the highest calorific values and intense gas formation are recorded in fuel with a high polyethylene content.

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ECOLOGY AND SUSTAINABLE DEVELOPMENT. ENVIRONMENTAL PROTECTION

Increase the Reliability and Accuracy of Assessing the Ecological State of a Surface Water Body's Sub-Basin

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Abstract. The article investigates the impact of surface water bodies in the Dnipro River sub-basins, in particular, the impact of the upstream tributary on the ecological state of the downstream main river. Such studies are necessary to establish the factors influencing the composition of river waters and to determine the ecological status of surface water bodies, including the left tributaries of the Dnipro, such as the Desna, Sula, Psel, and Vorskla.

Keywords: basin management principle, chloride and sulphate content, ecological state, impact of tributaries on water quality, surface water bodies.

Introduction

Studies of the ecological status of surface water bodies in the Dnipro basin have been conducted on numerous occasions, revealing a tendency for the Dnipro River to deteriorate due to anthropogenic pressure. However, the water quality of the Dnipro River is additionally affected by its tributaries, as shown in previous studies [1].

Groundwater is recharged by infiltration of precipitation, filtration from rivers, lakes, canals, and condensation of water vapor. During rains and spring snowmelt, their level rises, and during droughts and winter, it decreases. The connection with surface water bodies is that groundwater can recharge surface water and, therefore, be an additional source of pollution. The water content in the soil determines the intensity of biological, chemical, and physicochemical processes, the formation of the soil profile, water-air, nutrient, and thermal regimes, and its physical and mechanical properties.

The content of sulfates in natural waters varies widely and is caused by the leaching of sulfate-containing rocks or the discharge of industrial and domestic wastewater into water bodies. The main source of sulfates in surface waters is the chemical weathering and dissolution of sulfur-containing minerals, mainly gypsum, as well as the oxidation of sulfides and sulfur. Significant amounts of sulphates enter water bodies as a result of the death of organisms, oxidation of terrestrial and aquatic substances of plant and animal origin, and underground runoff. Most sulfates are highly soluble in water, except for barium sulfate (BaSO_4), which is insoluble in water, calcium sulfate (CaSO_4), silver sulfate (Ag_2SO_4), and lead sulfate (PbSO_4), which are poorly soluble. In turn, most chlorides are highly soluble in water and are not food for biological organisms. One of the sources of chloride discharges into surface water bodies is water supply and wastewater treatment plants.

Setting the task and solving it

In previous studies [2], [3], it was assumed that geographically upstream tributaries have an impact on downstream ones, and a search was launched for correlations between the chloride concentrations of the left tributaries of the Dnipro (Desna, Sula, Psel, Vorskla, and Samara) at the

observation posts closest to the Dnipro, determined by surface water monitoring data for 2013, 2016, and 2020.

The purpose of the study is to increase the level of **reliability and accuracy** of the assessment of the ecological state of the sub-basin of a surface water body by taking into account the mutual influence of the Dnipro's left tributaries on the change in the ecological state of the main waterway. To achieve **this goal, the following tasks must be solved:**

- **to investigate** the possible impact of water quality in the upstream left tributaries of the Dnipro on the downstream ones and on changes in the ecological status of the main waterway;
- **to develop** a mathematical model for predicting changes in the ecological status of surface water bodies within the sub-basin;
- **to develop** recommendations for managing the ecological status of surface water bodies.

The object of the study is the sub-basins of the left tributaries of the Dnipro River (the Desna River sub-basin, the Sula, the Psel, and the Vorskla River sub-basin of the Middle Dnipro) and their impact on the changing ecological state of the main waterway. The subject of the study is **the determination of general patterns** of ecological impact of the Dnipro's left tributaries within the basin on changes in the ecological state of the main waterway.

The scientific novelty **of the study is that:**

For the first time, the impact of a geographically upstream tributary on **downstream sections** of the main river was investigated by identifying the presence of an internal flow that ensures this impact.

For the first time, a mathematical model for predicting changes in the ecological state of a surface water body within a sub-basin was developed, **which makes it possible to predict** the impact of a geographically upstream tributary on downstream tributaries of the main river within the sub-basin.

To **confirm** the existence of an internal flow **facilitating** the influence of upstream tributaries on downstream ones, isolines were constructed based on monitoring data from the State Agency of Water Resources of Ukraine on the content of chlorides and sulphates in the tributaries of the Desna (6 observation sites), Sula (4 observation sites), Psel (6 observation sites), and Vorskla (4 observation sites) using publicly available geographic information system software QGIS (Quantum GIS – <https://www.qgis.org/>).

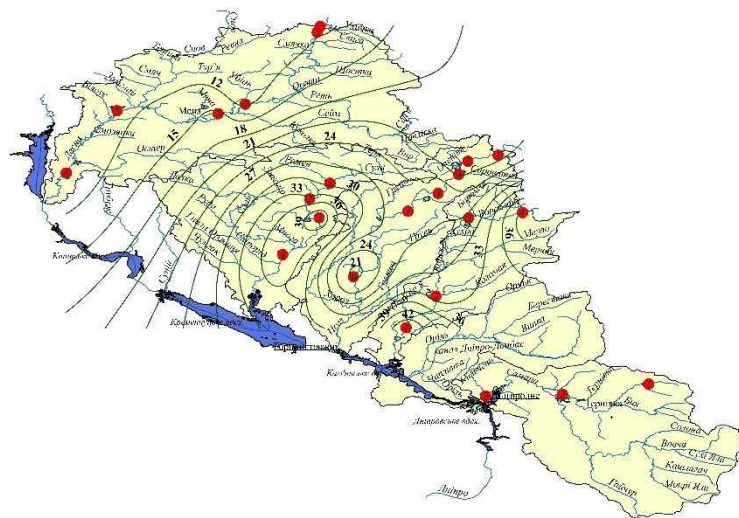


Fig. 1. Map of the distribution of chloride concentrations (mg/dm^3) in the basins of the Desna, Sula, Psel, and Vorskla rivers as of 2023 (in the original language).

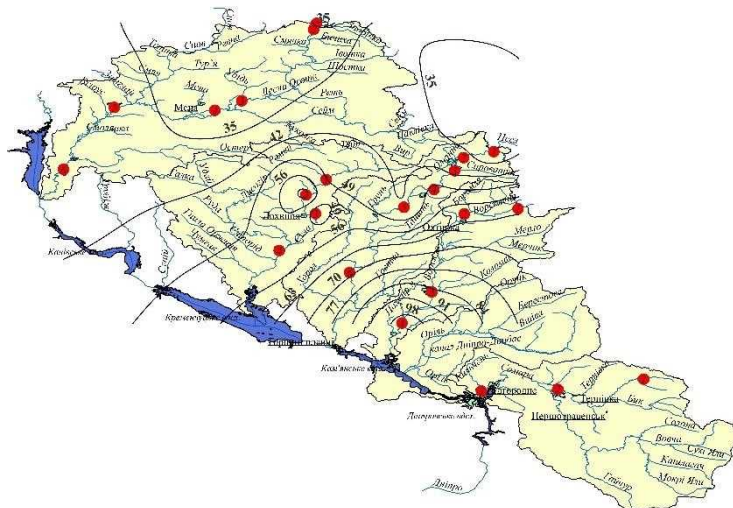


Fig. 2. Map of the distribution of sulphate concentrations (mg/dm³) in the basins of the Desna, Sula, Psel, and Vorskla rivers as of 2023 (in the original language).

The analysis of the results of the calculations presented in Figs. 1 and 2 shows that as the concentrations of chlorides and sulphates in the upstream tributaries of the Dnipro River increase, the concentrations in the downstream tributaries also increase. The isolines support the assumption that there is a groundwater influence between the tributaries, which contributes to changes in concentrations in the downstream tributary depending on changes in concentrations in the upstream tributary. A significant increase in chloride concentration is observed between gauging stations 3 and 4 of the Sula River, which may be due to the location of the Lubny Vodokanal facility of the Lubny City Council in Lubny and the Siaivo facility in Zasulia village, Lubny district, Poltava region, which, according to the environmental passport of the Poltava region, are pollutants of the surface water body.

To confirm the hypothesis, we searched for correlations between the chloride and sulphate concentrations of upstream tributaries and the tributaries located downstream of the main river along its course. For example, Figs. 3 to 8 shows the correlation between chloride and sulphate concentrations in tributaries in 2023.

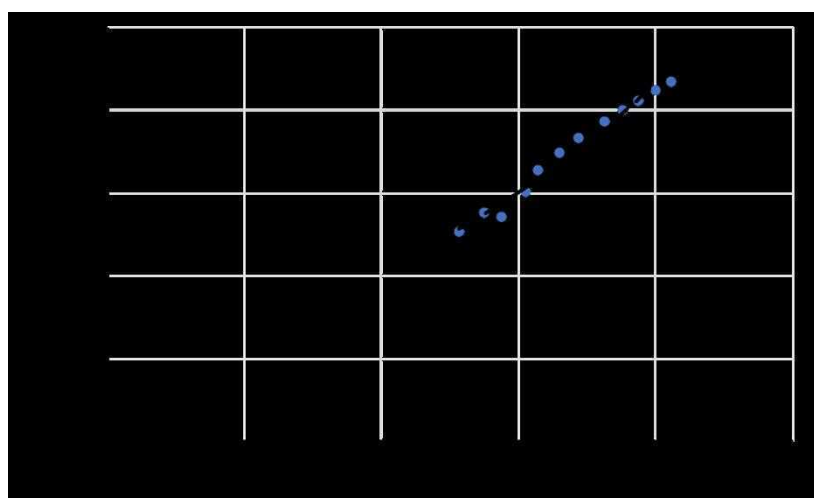


Fig. 3. Correlation of chloride content between the Desna (post 3) and Sula (post 1) tributaries in 2023.

The regression equation of the identified dependence $y = 10,148e^{0,091x}$ the reliability of the approximation $R^2 = 0,973$.

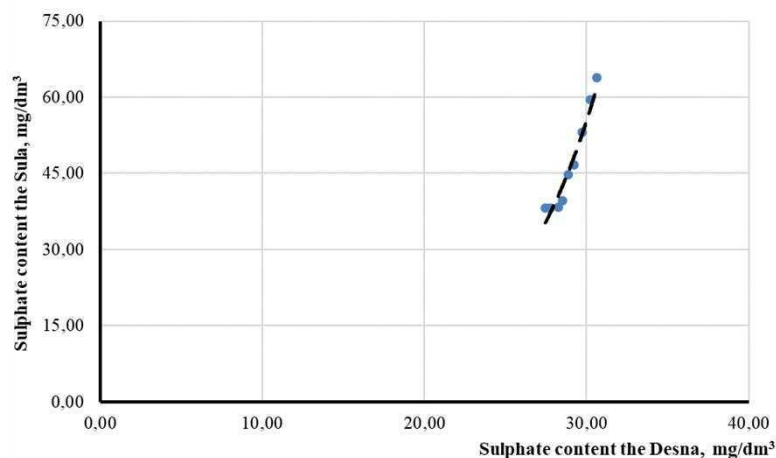


Fig. 4. Correlation of sulphate content between the Desna (post 3) and Sula (post 1) tributaries in 2023.

The regression equation of the identified dependence $y = 0,2696e^{0,1775x}$ the reliability of the approximation $R^2 = 0,9604$.

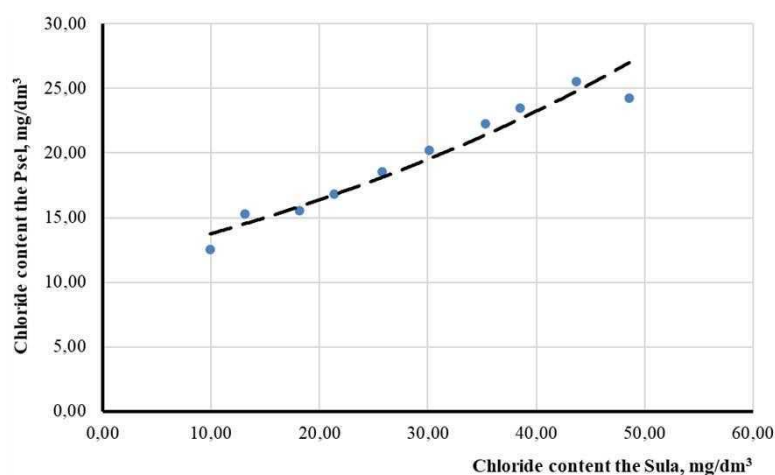


Fig. 5. Correlation of chloride content between the tributaries of the Sula (post 3) and Psel (post 6) for 2023.

The regression equation of the identified dependence $y = 11,547e^{0,0175x}$ the reliability of the approximation $R^2 = 0,931$.

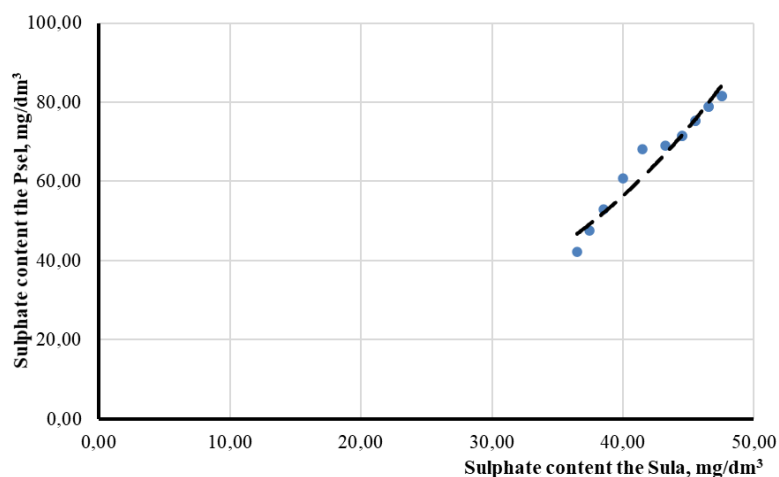


Fig. 6. Correlation of sulphate content between the tributaries of the Sula (post 3) and Psel (post 6) for 2023.

The regression equation of the identified dependence $y = 6,6643e^{0,0534x}$ the reliability of the approximation $R^2 = 0,9472$.

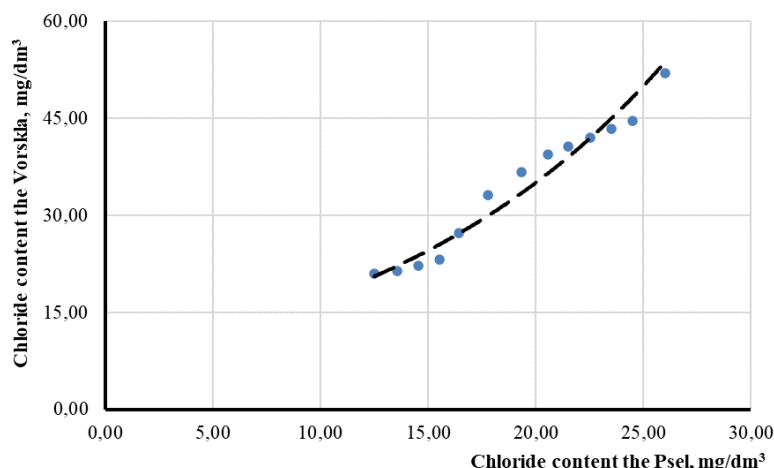


Fig. 7. Correlation of chloride content between the Psel (post 6) and Vorskla (post 4) tributaries in 2023.

The regression equation of the identified dependence $y = 8,4655e^{0,071x}$ the reliability of the approximation $R^2 = 0,9554$.

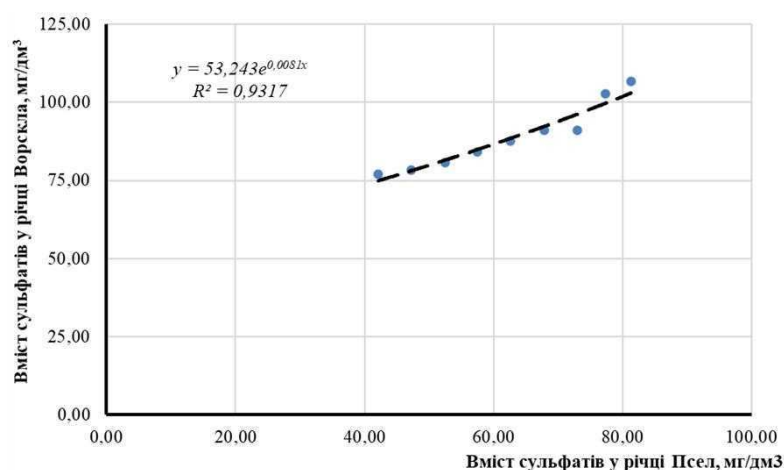


Fig. 8. Correlation of sulphate content between the Psel (post 6) and Vorskla (post 4) tributaries in 2023.

The regression equation of the identified dependence $y = 53,243e^{0,0081x}$ the reliability of the approximation $R^2 = 0,9317$.

The functional dependence on the concentrations of various impurities can be expressed using Eq. (1)

$$\psi = f(C_i; C_j), \quad (1)$$

where C_i, C_j are the concentrations of pollutants in different tributaries.

Since most natural processes, such as infiltration, water dilution, river self-purification, etc., can be described by an exponential law, it is reasonable to consider the process of influence of upstream tributaries on downstream ones based on this model.

The functional dependence will be in the form of Eq. (2):

$$y = a \cdot e^{bx}, \quad (2)$$

where a is a coefficient that characterizes the impact of the geological component, the degree of under-treatment of discharges in the areas of tributaries; b is a coefficient that characterizes the permeability of soils, which depends on the composition, structure, organic matter content, etc; x is the actual value of the pollutant concentration in the upstream tributary, mg/dm³.

The reproducibility of the experiments was checked by the Student's criterion Eq. (3).

$$t = \frac{\bar{x} - \bar{y}}{\sqrt{\frac{s_1^2}{n_1} + \frac{s_2^2}{n_2}}} \leq t_{(0,05;f_x)}, \quad (3)$$

where s^2 is the variance of the mean values, which is calculated using Eq. (4); $\bar{x} - \bar{y}$ is difference in sample means; $t_{(0,05;f_x)}$ is the tabulated value of the Student's t-test at the 5% significance level; $f_x = n - 1$ is number of degrees of freedom.

$$s = \frac{\sum_{i=1}^{n_1} (x_i - \bar{x})^2 + \sum_{i=1}^{n_2} (y_i - \bar{y})^2}{n_1 + n_2 - 2}. \quad (4)$$

The process is considered reproducible if inequality Eq. (3) is satisfied, while any Student's value obtained by calculation from the experimental data is less than its tabulated value.

The results of the calculation of the Student's criterion suggest that the hypothesis of exponential dependence is not rejected, since the calculated values of the criteria are less than the tabulated ones. The probability that the process of influence of upstream tributaries on downstream tributaries can be described by an exponential law is greater than 95%.

The basis of the proposed management algorithm actions for the implementation of the basin principle of water resources management is an integrated approach to assessing the ecological status of a surface water sub-basin by taking into account the impact of the Dnipro River's left tributaries on the ecological status of the main waterway. This algorithm involves the following steps: collection and processing of data by each involved entity, determination of the predicted impact of upstream tributaries on downstream tributaries of the main river within the sub-basin, which is a key factor in improving the reliability of the assessment of the environmental status of the surface water body sub-basin, identification of pollution sources, development and implementation of measures to prevent and eliminate negative consequences. To predict the ecological status of surface water bodies within a sub-basin, a mathematical model should be used, taking into account the impact of upstream tributaries on downstream tributaries, the reliability and adequacy of which have been proven by research.

When deciding on the necessary response measures to pollution of a downstream surface water body as a result of the impact of a water body that is geographically located upstream, it is recommended to proceed from the following. It is assumed that, according to the information on potentially possible pollution or existing pollution of a water body, structural units, using possible means of communication, should, as soon as possible, bring information on the situation to each involved organization that monitors the environmental condition of water bodies: basin water resource management, territorial units of the State Emergency Service of Ukraine, the State Environmental Inspectorate, and local executive authorities.

These structures, independently or in cooperation with another organisation (polluting enterprise), should immediately take the necessary measures to inspect and clarify the situation, to

eliminate the consequences, and control the situation that has arisen in the water body. The organisations responsible for developing and monitoring the implementation of response measures and the enterprises that comply with the issued orders shall organise continuous monitoring of the situation in order to establish the effectiveness of the developed measures and promptly notify all interested parties in accordance with the established procedure, informing them of the ecological state of the water body, the concentrations of pollutants in it and in the enterprise's wastewater, including the expected concentration values from geographically upstream rivers, the actions taken and the If the maximum permissible concentration is exceeded, the information is immediately transmitted to the territorial bodies of the State Emergency Service of Ukraine to determine the scale of the situation and assess the threat to the life of the population in a particular area, which in turn promptly communicate the information to the population and local authorities.

Conclusions

Based on the constructed isolines of sulphate and chloride concentrations, it **has been proven that pollutants from a geographically upstream tributary of the main river impact the downstream tributary. It has been established** that the influence of upstream tributaries on downstream tributaries **follows** an exponential law.

The constructed mathematical model **enables** predicting the impact of upstream tributaries on downstream ones. The developed model for predicting the ecological state of surface water bodies in the Dnipro sub-basins is **both reliable and efficient**, and it can be implemented in calculating the risk of **natural and anthropogenic** disasters, since the calculated values of **Student's criterion** are less than **the corresponding tabulated values**.

The implementation of the proposed model for predicting the ecological state of a water source, taking into account the influence of upstream tributaries, will **enhance** the management of the ecological state of a surface water body **at the basin level**.

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Fusel Oil and the Ecology of Road Transport

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Abstract. *This article analyzes the impact of alcohol waste on motor fuels' ecological parameters. Adding alcohol waste improves engine starting, fuel evaporation, and combustion. Fusel oil reduces emissions in carburetor engines (5-7% optimal) and improves diesel fuel (10-12% optimal), reducing density and viscosity and increasing cetane index.*

Keywords: fusel oil, ecology, carburetor engine, diesel engine, gasoline, cetane index, diesel fuel.

Introduction

Vehicle emissions significantly harm air quality and human health. The increasing number of vehicles on the roads has led to stricter fuel regulations worldwide, with billions of dollars being spent on initiatives aimed at reducing harmful emissions, as evidenced by international agreements like the Kyoto Protocol. Road transport is a major environmental polluter, releasing a variety of toxic substances, including carbon monoxide, nitrogen oxides, and hydrocarbons. These pollutants contribute to air pollution, respiratory diseases, and climate change. Table 1 provides a detailed breakdown of the composition of exhaust gases from both carburetor and diesel engines, highlighting the presence of toxic components like carbon monoxide and nitrogen oxides [1].

Table 1

Composition of exhaust gases from carburetor and diesel engines

Components of engine exhaust gases	Concentration of exhaust gases in engines, % vol.		Note
	carburetor	diesel	
1. Nitrogen	74.00 -77.00	76.00 – 78.00	non-toxic
2. Oxygen	0.300 – 8.000	2.0 – 18.000	non-toxic
3. Water vapor	3.000 – 5.500	0.5 – 4.000	non-toxic
4. Carbon dioxide	5.000 – 12.000	1.0 – 10.000	non-toxic
5. Carbon monoxide	0.100 – 10.000	0.01 – 5.000	toxic
6. Nitrogen oxides	0.010 – 0.800	0.004 – 0.060	toxic
7. Sulfur dioxide	0 - 0.002	0 - 0.030	toxic
8. Hydrocarbons	0.200 - 3.000	0.009 - 0.500	toxic
9. Aldehydes	0 - 0.200	0.001 - 0.009	toxic
10. Soot	0 - 0.040	0.010 - 1.100	toxic
11. Benzopyrene	0.010 - 0.020	up to 0.010	toxic

Carburetor engines are known to primarily release toxic carbon monoxide and nitrogen oxides. The use of high-octane gasoline, which contains a high concentration of aromatic compounds, has been shown to increase the emissions of benzopyrene. Diesel engines, on the other hand, tend to burn fuel more completely, resulting in fewer unburned hydrocarbons. However, they often produce higher amounts of sulfur dioxide and soot due to a weaker air supply. Despite

this, diesel engines generally consume less fuel and emit fewer overall exhaust gases compared to gasoline engines of the same power output. It is crucial to note that complete fuel combustion in all engine types is essential for significantly reducing harmful emissions [1-3].

There is a well-established European system for regulating the quality of automotive fuel, which classifies fuels into different ecological classes. Currently, the release of Euro-3, Euro-4, and Euro-5 fuel classes is regulated within the European Union. The specific requirements for each fuel class are determined by technical regulations. The latest environmental standard, Euro-6, was introduced in Europe in 2015. This standard represents a significant step forward in the development of diesel technologies, with a strong focus on reducing the environmental impact of diesel engines and improving the overall quality of diesel fuel.

The main aspects of the Euro standards for motor fuels include:

- 1) Strict control over the quality of the fuel used. This ensures that fuels meet specific environmental and performance criteria.
- 2) Limiting the level of sulfur in diesel fuel and reducing emissions of harmful sulfur compounds that contribute to air pollution. Sulfur dioxide emissions are a major concern due to their contribution to acid rain and respiratory problems [3].

Restrictions on emissions of nitrogen oxides and particulate matter require the use of advanced exhaust gas purification technologies and the improvement of combustion systems. These restrictions drive innovation in engine design and emission control.

Control over the completeness of fuel indicators, which are important for ensuring their cleaner and faster combustion, thereby helping to reduce harmful emissions. Comprehensive monitoring of fuel properties ensures optimal performance and minimal environmental impact.

In conclusion, Euro-standard motor fuels, with their advanced environmental standards and strict emission regulations, are a vital step towards achieving a cleaner and more sustainable future for road transport. These standards not only reduce the harmful impact of vehicles on the environment but also increase the efficiency and productivity of engines.

The main factors that influence the combustion process in a carburetor engine include: the time it takes to prepare the combustible mixture, environmental parameters such as temperature and pressure, the thermal state of the engine, and the quality of the fuel used. Higher environmental temperature and pressure, along with a favorable thermal state of the engine, contribute to more complete fuel evaporation and a better quality of the combustible mixture [4,5]. An important direction for further improvement of the carburetor engine power system is to ensure the maximum possible evaporation of fuel before it enters the cylinder. To evaluate this parameter, the point of fractional distillation of gasoline – specifically, the boiling point of 50% by volume – is used. This point characterizes the completeness of fuel evaporation, the engine's quick transition from one operating mode to another, and the uniform distribution of fuel among the cylinders.

Other indicators of carburetor engine fuels that affect the environment include: the boiling point of 10% of the fuel, which improves the starting properties of the engine in cold conditions and influences its tendency to form gas plugs in the system; and the boiling points of 90% and the end of fuel boiling, which positively affect the completeness of its combustion and the uniformity of its supply to the engine cylinders.

Modern diesel fuel must meet numerous requirements to ensure reliable engine operation. The most important of these include: good fuel spraying and optimal mixture formation; complete combustion of fuel with a short ignition delay and minimal formation of soot and toxic substances; the ability to pump fuel effectively to ensure reliable and uninterrupted operation of the fuel

system; low resin formation in the combustion chamber; no corrosion of fuel system parts; and stability of technological properties during long-term storage [6].

The main operational indicators of diesel fuel that, to varying degrees, affect the environment include: cetane number (cetane index), fractional composition, viscosity, density, and the presence of sulfur compounds [6].

The cetane number and cetane index characterize the ignitability of diesel fuel, which affects the presence of harmful components in exhaust gases, such as CO and CH. A shorter ignition delay period means the fuel burns faster. This speeds up engine operation and increases its power, which in turn reduces the content of harmful components in the exhaust gases. The reduction in the ignition delay period depends on the rate of hydrocarbon oxidation during the reactions that occur before the rapid combustion phase. If the pre-flame reactions proceed slowly, the ignition delay period increases, resulting in fuel accumulating in the cylinder and then igniting a significant amount at once. A decrease in the cetane number worsens the performance of the diesel's operating cycle, noticeably increasing the harshness of operation and wear of engine parts. If its value drops below 40 units, starting the engine becomes problematic even in warm weather due to the increased self-ignition temperature of the fuel.

Indicators such as viscosity and density determine the level of evaporation and mixture formation of diesel fuel, as well as the degree of its spraying in the combustion chamber. Denser and more viscous fuel ignites and burns worse, which leads to higher diesel fuel consumption and smoke in the exhaust gases. For all types of engines, a characteristic feature can be noted: the denser the diesel fuel, the higher the total content of aromatic hydrocarbons, and the more harmful compounds such as pyrene and benzopyrene are contained in the exhaust [7].

The fractional composition of diesel fuel determines the completeness of its combustion, the smoke, and the toxicity of the engine's exhaust gases. An analysis of the fuel fractional distillation points that affect the environment will be considered below.

Many methods for optimizing the ecological parameters of motor fuels are discussed in the scientific literature.

It is known that the operation of a car in low ambient air temperatures leads to a deterioration of the engine's thermal state, which has a significant impact on increasing fuel consumption (by 10...30% or more) and, as a result, increasing the emission of harmful substances with exhaust gases. In this case, the increase in fuel consumption is associated with an increase in fuel viscosity, a deterioration in its ability to spray and evaporate. Fusel oil, an alcohol production by-product, can be used to create high-octane additives, offering a method to improve fuel ecological parameters and reduce waste [7-13].

Research Methodology

For experimental studies, a straight-run fraction of gasoline and diesel fuel after atmospheric distillation was used, as well as fusel oil (FO) – a waste product of alcohol production. Fusel oil contains a mixture of higher alcohols (isoamyl, isobutyl, n-propyl, ethyl), water, and a small amount of esters.

The study was conducted in two stages – studying the effect of FO on the ecological parameters of gasoline (1st stage) and studying the effect of FO on the ecological parameters of diesel fuel (2nd stage). In the first stage, mixtures of gasoline with fusel oil (FO) additives were prepared in the following volumetric proportions:

1. gasoline (100%) + FO (0%), 2. gasoline (95%) + FO (5%),
2. gasoline (94%) + FO (6%), 4. gasoline (92.5%) + FO (7.5%),
3. gasoline (90%) + FO (10%), 6. gasoline (85%) + FO (15%).

Distillation of gasoline and prepared mixtures was carried out, during which their fractional composition was determined, namely: the boiling points of the 10%-, 50%-, 90%-points, and the final boiling point [14]. The obtained fractional compositions were analyzed to determine.

In the second stage, mixtures of diesel fuel (DF) with fusel oil (FO) additives were prepared in the following volumetric proportions:

1. DF (100%) + FO (0%), 4. DF (90%) + FO (10%),
2. DF (95%) + FO (5%), 5. DF (88%) + FO (12%),
3. DF (92%) + FO (8%), 6. DF (85%) + FO (15%).

For the resulting mixtures, the density ρ_{15} was determined by the pycnometric method, and the kinematic viscosity ν by a capillary viscometer. After that, distillation of diesel fuel and prepared mixtures was carried out, during which their fractional composition was determined, namely: the initial boiling point, and boiling points of the 10%- and 50%-points. The obtained fractional compositions were analyzed, and the cetane indices for the analyzed samples were determined.

For diesel fuels, the main parameters characterizing the ignition delay period of the fuel-air mixture under compression are the cetane number and the cetane index (CI) – an indicator used in European standards.

The CI was determined according to DSTU ISO 4264:2009 (ISO 4264:1995, IDT) by a method that consists of determining the density of diesel fuel at 15°C and the average boiling point of 50% (by volume) of its quantity. The cetane index was calculated using the formula:

$$CI = 454.74 - 1641.416 \rho + 774.74 \rho^2 - 0.554 T_{50\%} + 97.803 (\lg T_{50\%})^2,$$

where ρ – diesel fuel density at 15°C, g/cm³;

$T_{50\%}$ – boiling point of 50% (by volume) of the analyzed mixture, °C.

Results and Discussion

The research initially focused on how fusel oil affects the fuel mixture's fractional composition, specifically analyzing how changes in boiling points impact gasoline's ecological properties. Experimental results (Table 2) indicated that alcohol waste influences fuel parameters for carburetor engines, including the 10%, 50%, and 90% boiling points, as well as the final boiling point.

Table 2

Main characteristics of the fuel mixture with fusel oil (FO) additives for assessing the ecology of a carburetor engine

Fuel mixture content, % vol.		Main characteristics of the fuel mixture				
Gasoline	CO	$\rho_{4^{20}}$	$T_{10\%},$ °C	$T_{50\%},$ °C	$T_{90\%},$ °C	$T_{KK},$ °C
100	-	0,7633	80	130	174	174
95	5	0,7653	62	118	172	172
94	6	0,7263	53	87	160	155
92,5	7,5	0,7663	88	125	157	157
90	10	0,7674	98	127	158	160
85	15	0,7688	98	130	170	175

Adding fusel oil lowers the fuel's 10% boiling point (Fig. 1), which enhances engine starting in cold weather and reduces vapor lock formation. Consequently, it shortens the time needed to prepare the fuel-air mixture during cold periods, leading to fewer harmful emissions. The ideal fusel oil concentration in the fuel blend is between 5-7% by volume (Fig. 2).

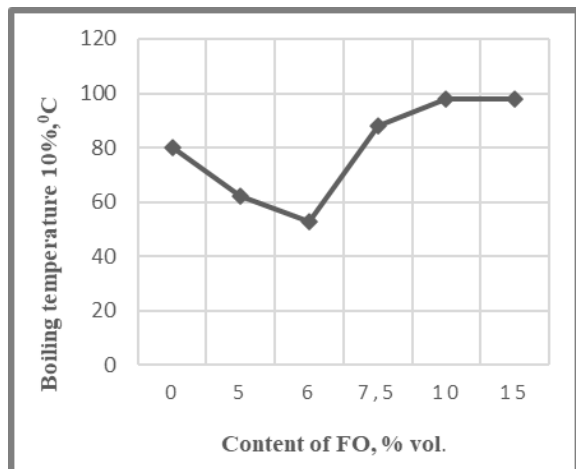


Fig. 1. Dependence of the boiling point of the 10% fraction of the fuel mixture on the concentration of fusel oil (FO) in gasoline

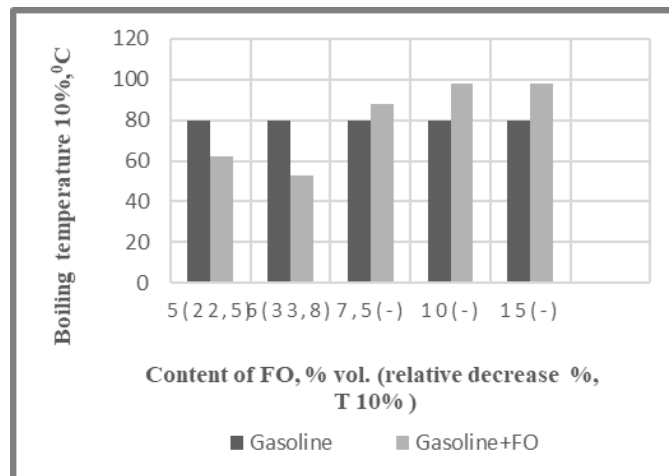


Fig. 2. Comparison of boiling points of the 10% fraction of gasoline and the fuel mixture (Gasoline + Fusel Oil) at different concentrations of fusel oil in gasoline.

For cleaner emissions, fuel should evaporate well before entering the engine cylinder. The 50% boiling point ($T_{50\%}$) indicates this. Adding fusel oil lowers the $T_{50\%}$, improving evaporation, engine responsiveness, and fuel distribution among cylinders (Fig. 3 & 4).

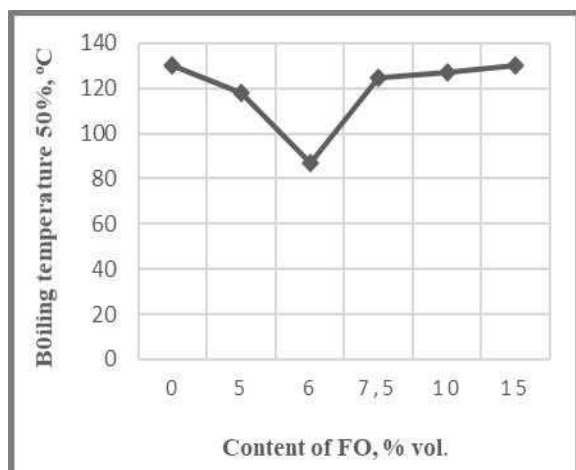


Fig. 3. Dependence of the boiling point of the 50% fraction of the fuel mixture on the concentration of fusel oil (FO) in gasoline

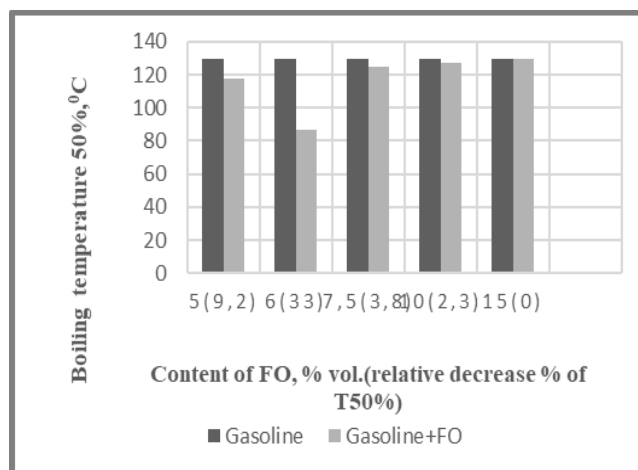


Fig. 4. Comparison of boiling points of the 50% fraction of gasoline and the fuel mixture (Gasoline + Fusel Oil) at different concentrations of Fusel Oil in gasoline.

Fusel oil lowers the fuel's 90% and final boiling points, improving combustion and fuel delivery to engine cylinders (Fig. 5). This reduces carbon monoxide and nitrogen oxide emissions. The ideal fusel oil concentration is 6-10% by volume (Fig. 6).

The results of the experimental and calculated data, which were determined for diesel fuel and its mixtures with fusel oil additives, are presented in Table 3. The results provided were used to analyze the main operational and ecological indicators of the fuel mixtures.

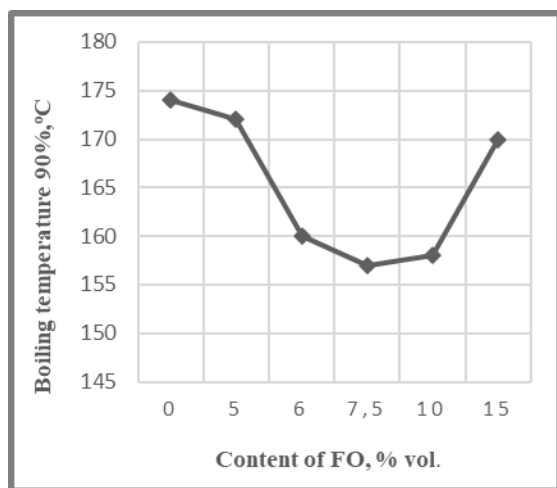


Fig. 5. Dependence of the boiling point of the 90% fraction of the fuel mixture on the concentration of fusel oil (FO) in gasoline

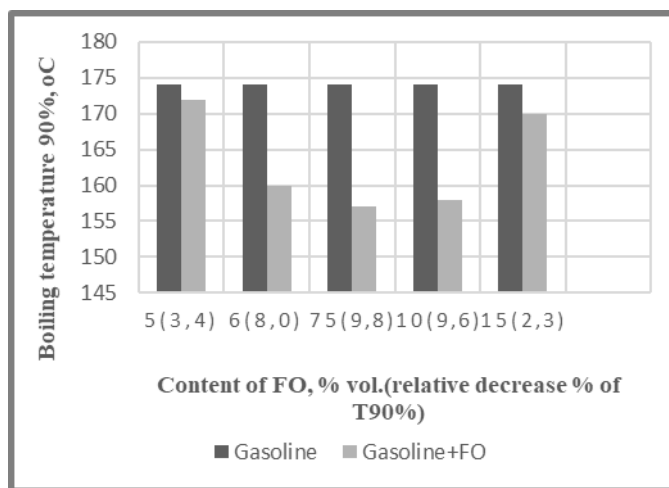


Fig. 6. Comparison of boiling points of the 90% fraction of gasoline and the fuel mixture (Gasoline + Fusel Oil) at different concentrations of fusel oil in gasoline.

Table 3

Main characteristics of the fuel mixture with fusel oil (FO) additives for assessing the ecology of a diesel engine

Fuel mixture content, % vol.		Main characteristics of the fuel mixture					
DF, %vol.	FO, %vol.	v_{20} , cCt	ρ_{15} , kg/m ³	$T_{пк}$, °C	T_{10} , °C	T_{50} , °C	CI
100	-	4.05	835.52	94	208	277	42.53
95	5	3.84	807.42	90	165	275	43.75
92	8	3.45	802.65	91	148	270	45.59
90	10	3.42	802.73	92	151	271	46.84
88	12	3.39	801.66	93	172	272	47.26
85	15	3.39	801.45	93	183	281	46.87

Diesel fuel viscosity and density significantly impact environmental performance. Lower viscosity improves fuel atomization, ignition, and combustion, leading to reduced fuel consumption and emissions. Conversely, higher viscosity hinders these processes, resulting in increased fuel use and exhaust smoke. Reduced fuel density also lowers the mass flow rate during engine operation.

Figure 7 shows that adding fusel oil (FO) to diesel fuel decreases both density and viscosity proportionally. This positively affects the previously mentioned indicators. The decrease begins with the initial FO concentration and stabilizes at 10-15% by volume. Within this optimal range, viscosity drops by 19% and density by 4% compared to pure diesel fuel. Figure 8 illustrates the percentage decrease in density with varying FO amounts.

Diesel fuel density also indicates aromatic hydrocarbon content. These hydrocarbons can form harmful substances like pyrene and benzopyrene during combustion, polluting the air. Studies show that decreasing diesel fuel density from 860-870 to 800 kg/m³ reduces aromatic hydrocarbons from approximately 27% to 15%. Based on this, the 4% density reduction in our case suggests a 6-9% decrease in aromatic hydrocarbons, which improves the composition of engine exhaust gases.

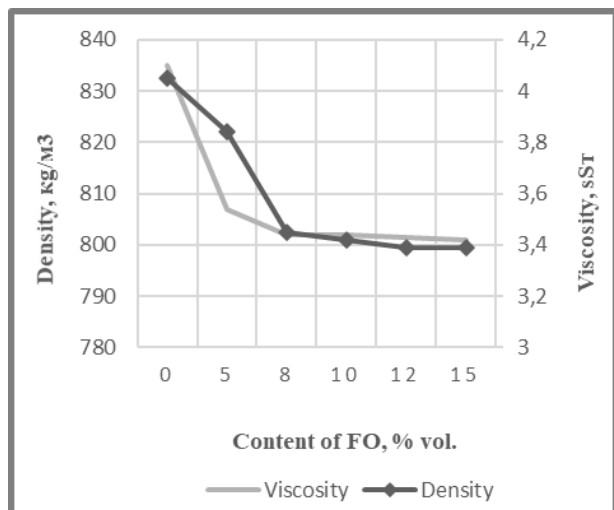


Fig. 7. Dependence of density and viscosity of the fuel mixture on the concentration of fusel oil (FO) in diesel fuel

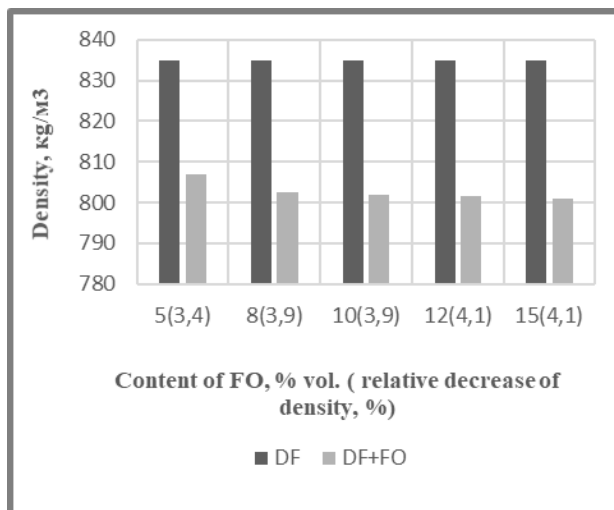


Fig. 8. Comparison of densities of diesel fuel (DF) and the fuel mixture (DF + Fusel Oil) at different concentrations of fusel oil in diesel fuel.

A key factor for cleaner diesel fuel combustion is the cetane index. A higher cetane index means faster pre-oxidation and ignition, leading to reduced harmful emissions. Euro diesel fuel should have a cetane index of at least 46.0.

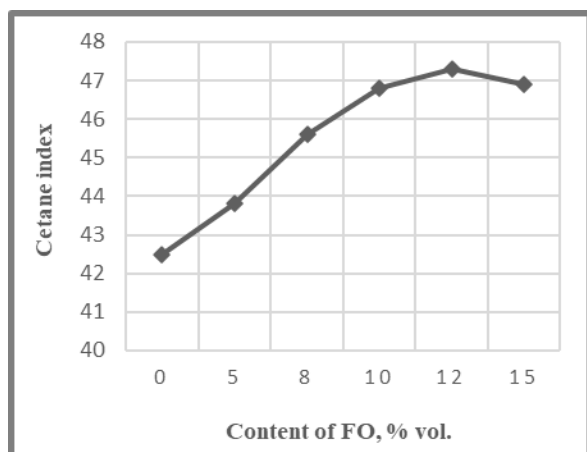


Fig. 9. Dependence of the cetane index of the fuel mixture on the concentration of fusel oil (FO) in diesel fuel.

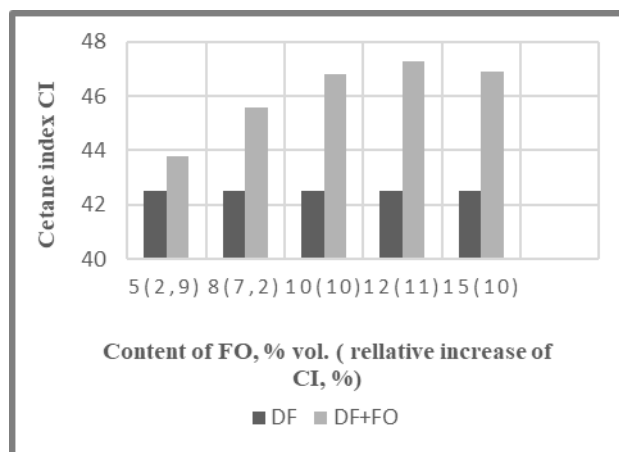


Fig. 10. Comparison of cetane indices of diesel fuel (DF) and the fuel mixture (DF + FO) at different concentrations of FO in diesel fuel.

Adding 10% fusel oil (FO) to diesel fuel meets Euro standards for cetane index (CI), while 12% FO raises it to 47.3 (Figs. 9 & 10). FO also lowers the 10% boiling point, improving cold starts and reducing emissions. The ideal FO concentration for this is 8-10% (Figs. 11 & 12).

A lower 50% boiling point (t_{50}) in diesel fuel improves engine warm-up speed, reduces fuel consumption, and enhances maneuverability, benefiting urban driving. Adding fusel oil (FO) significantly decreases t_{50} , with an optimal FO concentration of 10% by volume (Fig. 13 & 14).

Conclusions

Fusel oil, a byproduct of alcohol production, can be incorporated into motor fuels to lessen vehicle-related environmental pollution.

Adding fusel oil improves gasoline's fractional composition. It enhances engine starting in cold conditions, promotes fuel evaporation, and improves combustion completeness and fuel

distribution to engine cylinders. Such impact leads to a reduction in carbon monoxide and nitrogen oxide emissions. The ideal fusel oil concentration in gasoline is 5-7% by volume.

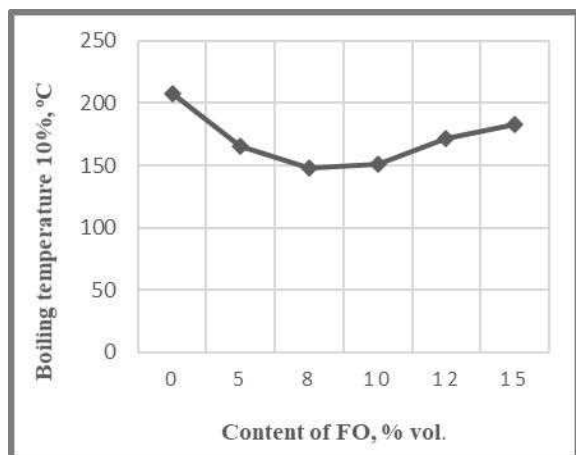


Fig. 11. Dependence of the boiling point of the 10% fraction of the fuel mixture on the concentration of fusel oil (FO) in diesel fuel.

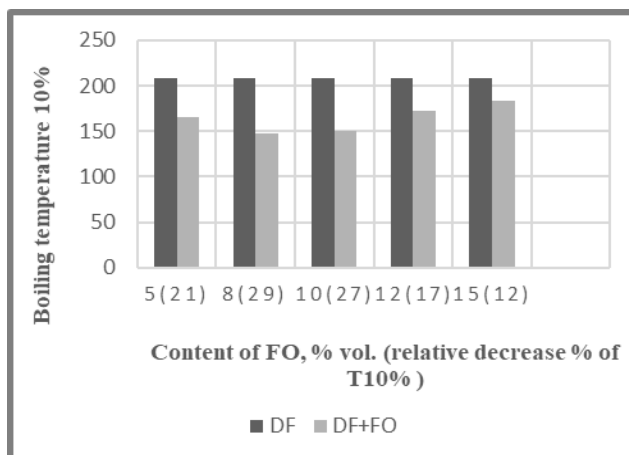


Fig. 12. Comparison of boiling points of the 10% fraction of diesel fuel (DF) and the fuel mixture (DF + Fusel Oil) at different concentrations of fusel oil in diesel fuel.

Fusel oil also positively impacts diesel fuel's ecological parameters. It lowers fuel density and viscosity, aiding in spraying, ignition, and combustion, leading to reduced fuel consumption. Lowering fuel density can decrease aromatic hydrocarbon content, improving exhaust gas composition. Fusel oil increases the cetane index, promoting cleaner and faster combustion and reducing harmful emissions. It also lowers the 10% and 50% boiling points of the fuel mixture, improving engine operation in various modes, easing cold starts, and enhancing maneuverability. This reduces carbon monoxide and nitrogen oxide emissions.

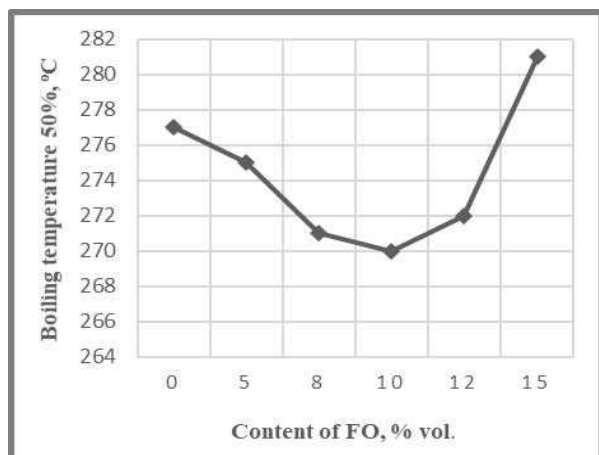


Fig. 13. Dependence of the boiling point of the 50% fraction of the fuel mixture on the concentration of fusel oil (FO) in diesel fuel

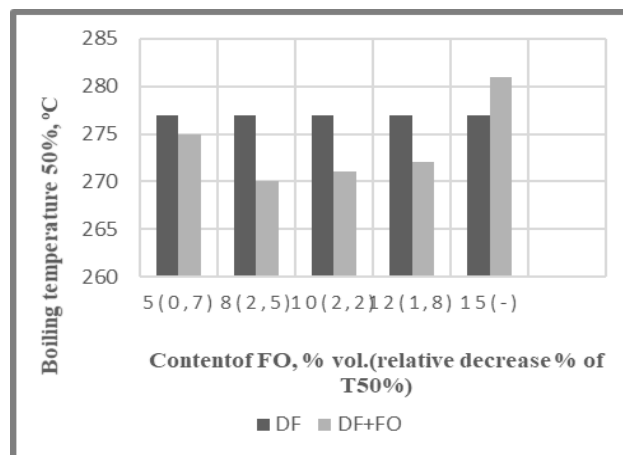


Fig. 14. Comparison of boiling points of the 50% fraction of diesel fuel (DF) and the fuel mixture (DF + Fusel Oil) at different concentrations of fusel oil in diesel fuel.

Adding fusel oil to diesel fuels enhances their ecological parameters and helps them meet Euro standards. The optimal fusel oil concentration in diesel fuel is 10-12% by volume.

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Evaluation of the Influence of Biosurfactants, Microbial Preparation, Sorbents on the Adaptive Capacity of Rye During Growth on Oil-Contaminated Soil

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Abstract. It has been established that biosurfactants, microbial preparations, natural sorbents, and oxidants increase the content of photosynthetic pigments in rye when grown on oil-contaminated soils. Developed an integrated approach that contributes to increasing plants' adaptive capacity, neutralizing the negative impact of the environment. Proposed methods are promising for the phytoremediation of oil-contaminated soils and damage as a result of military operations.

Keywords: biosurfactants, microbial preparation, natural sorbents, oxidants, photosynthetic plant pigments, oil-contaminated soil.

Introduction

Today, an important environmental problem is the increase of technogenic impact caused by the activities of oil enterprises, in particular in the process of production, processing, transportation, and storage of oil and oil products [1]. Oil and its derivatives, when released into the environment, adversely affect the water regime, change the physical and chemical properties of soils (leading to the transformation of their humus state, acid-base, redox and cation exchange properties), reduce biological activity, the content of nutrients: nitrogen, phosphorus and potassium, which leads to the suppression of microbiota, vegetation, and reduced soil fertility [2]. Therefore, it is an urgent task to find new ways to neutralise the negative impact of oil pollution on plants, increase their adaptive capacity for environmental remediation.

Surface-active products of microbial synthesis – biosurfactants – are promising activators for soil rehabilitation [3]. Due to biosurfactants functional properties (surface, emulsifying activity, effect on permeability of plant and microbial cell membranes, activity at low concentrations, different pH, temperatures), as well as biodegradability, they are advisable to use in modern technologies to increase plant adaptation to pollution and restore soil fertility [4–8].

It is known that the impact of oil and oil products changes a number of soil microorganisms of the main physiological groups, in particular microorganisms of the root zones of plants, which

occupy a special place among natural factors of soil quality [9]. Hydrocarbon-degrading microorganisms play a crucial role in the processes of soil self-purification from oil and oil products. They can use oil as a source of carbon, which allows them to influence the destruction of pollutants in the soil [10]. Introduced hydrocarbon-degrading microorganisms have high metabolic activity and oil consumption rate, and are competitive for long-term survival in changing environmental conditions [10]. Most of the known biotechnological treatment methods involve the use of pure and mixed cultures of microorganisms in combination with various substances or methods that stimulate their activity and create optimal conditions for their life [9, 11].

In order to accelerate the process of biodegradation (detoxification) of oil pollution and increase the activity of microbial degraders, inorganic, natural organic, organo-mineral, and synthetic sorbents are used. They should have high ion exchange and adsorption properties, while being environmentally safe, efficient, and economically feasible [12]. Natural sorbents are used in construction, industry, agriculture, and environmental protection [13]. To clean soils from various contaminants, use ion-exchange resins, clay minerals (glauconite, bentonite), silica, adsorbents modified with aminopolycarboxylic acids, basalt gravel, quartz sand, dolomite, calcium carbonate, manganese oxide (IV), activated carbon, anthracite, and others [13, 14]. Particular attention should be paid to clay minerals, which, due to their microporous structure, can absorb and retain large amounts of water and gradually release it [15, 16], which has a positive effect on the preservation of soil moisture for plants. Clay minerals contain physiologically necessary macro- and microelements for plant nutrition. Therefore, clay minerals are also promising complex fertilisers for enriching the soil with nutrients, improving its structure, retaining moisture, stimulating growth, and reducing plant diseases [15, 16]. Activated carbon (biochar), which is produced by pyrolysis of plant biomass and woodworking waste, is also used as a component for optimising plant growth [17]. Biochar has a developed porous structure, contains mobile organic matter that is easily biodegradable, improves agronomic and agrochemical properties of soils, increases the yield and quality of agricultural products, and contributes to solving the problem of climate change [18]. Due to its high adsorption capacity, biochar can provide detoxification of inorganic and organic contaminants of various natures. Another important potential remediation activator is calcium peroxide (CaO_2). Due to its wide range of functional properties, calcium peroxide belongs to the group of inorganic metal peroxides, which are known as sources of active oxygen. CaO_2 decomposes upon reaction with water, forming calcium hydroxide (Ca(OH)_2) and oxygen (O_2). This process promotes soil aeration and nutrient availability (N, P, K, Ca, Mg, S). This is especially beneficial for the development of plant root systems and microbial reducers that require oxygen for efficient decomposition of organic pollutants [19–21]. One of the main benefits of calcium peroxide is to improve soil structure by reducing its acidity (especially in acidified soils), which helps to optimize pH – an important factor for the vital activity of beneficial microflora and plant growth in a polluted environment [19].

Results and discussion

In experiments were used: artificially oil-contaminated soils (oil content – 5%), biosurfactants – rhamnolipid biocomplex (RBC) – a product of microbial synthesis of *Pseudomonas* sp. PS-17 and trehalosolipid surfactants (TL) of *Gordonia rubripertincta* strain UCM Ac-122, as well as a microbial preparation based on natural hydrocarbon destructors (D) from oil-contaminated areas, natural sorbents – glauconite, bentonite, activated birch charcoal (produced by pyrolysis of birch wood raw materials followed by activation with water vapour at a temperature of 800–950°C and subsequent crushing), calcium peroxide (CaO_2) as a source of oxygen for soil and microorganisms, and plants – rye (*Secale cereale* L.). In different variants of

the experiment, CaO_2 , natural sorbents, and microbial preparation D (50 ml of suspension, 5×10^6 CFU/cm³ per 1 kg of soil) were pre-applied to the soil, and after 14 days, rye seeds were planted, which were pre-sowing treatment (3 h) in solutions of RBC (0.01 g/dm³), TL (0.05 g/dm³), or H₂O (control). After that, we evaluated one of the parameters of plant response to changes in growing conditions and, at the same time, a bioindicator of the state of natural ecosystems, namely the quantitative content of photosynthetic pigments (chlorophylls) and carotenoids – the main photoreceptors of the photosynthetic cell. The content of photosynthetic pigments (chlorophylls) in plants is an important adaptive parameter that characterises the potential capacity of the photosynthetic apparatus, the reaction of plants to stress factors (photooxidative damage in plant chloroplasts), and is closely related to their productivity [22].

The content of photosynthetic pigments (chlorophyll *a*, chlorophyll *b*, and total carotenoids) in plant material was determined by the spectrophotometric method [23]. To isolate photosynthetic pigments from the experimental plants, 96% ethanol was used. The optical density of the obtained extracts was determined at wavelengths of 665, 649, and 440.5 nm. The concentration of chlorophylls was calculated using Vernon's formulas, and carotenoids by Wettstein [23]. The results were processed statistically.

It was found that the use of biosurfactants, microbial preparation, natural sorbents, and oxidants contributes to the increase of photosynthetic pigments content in sowing rye. The best results in terms of chlorophyll *a* content were obtained in the variants: TL + glauconite – 48.5%; RBC + D + glauconite + CaO_2 – 48.6%; TL + bentonite – 51%; TL + D + glauconite + CaO_2 – 51.6%; TL + D + coal – 51.8%; RBC + D + coal + CaO_2 – 49.3%; TL + D + coal + CaO_2 – 49.8%. compared to the control; in terms of chlorophyll *b* content: RBC + D + glauconite + CaO_2 – 48.8%; TL + D + bentonite + CaO_2 – 64.5%; RBC + D + coal + CaO_2 – 52.6%; TL + D + coal + CaO_2 – 68.6%; by total chlorophyll *a+b* content: RBC + D + glauconite + CaO_2 – 48.7%; TL + D + bentonite + CaO_2 – 58.3%; RBC + D + coal + CaO_2 – 51%; TL + D + coal + CaO_2 – 59.5%; by carotenoids: RBC + bentonite – 48.4%; TL + D + bentonite + CaO_2 – 47.1%, respectively.

Conclusion

Thus, the use of biosurfactants, microbial preparation, and natural sorbents promotes the oxidation of photosynthetic pigments in rye plants when growing on oil-contaminated soils. The best results in terms of total chlorophyll *a+b* content were in the variants: TL + D + bentonite + CaO_2 – 58.3%; RBC + D + coal + CaO_2 – 51%; TL + D + coal + CaO_2 – 59.5% compared to the control. This integrated approach may be promising for increasing plants' adaptive capacity, neutralizing the negative impact of environmental conditions, and increasing the phytoremediation efficiency of soils contaminated with oil and damaged as a result of military operations.

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The impact of Biochar Amendments and Biostimulant on Soil Nematodes and Biomass Yield of Miscanthus on Poor-Nutritionally Soils of Post-Military Areas in Kyiv Region

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Abstract. *This study investigates the influence of biochar and biostimulants on soil properties, nematode community structure, and Miscanthus yield in degraded post-military soils. BD2 treatment demonstrated the highest biomass production, while nematode trophic diversity stabilized over time. Future research should assess trace element interactions with nematode communities and Miscanthus yield dynamics.*

Keywords: biochar, biostimulants, nematodes, plant growth, yield, nematode community, trace elements.

Introduction

Finding cost-effective and eco-friendly ways to restore soil in post-military areas is essential [1,2]. One promising method is planting *Mischanthus × giganteus* (*M×g*), a high-biomass perennial grass. *Miscanthus* is well-known for its ability to tolerate poor soil conditions, including contamination with heavy metals. Plant stabilizes contaminated soils, preventing pollutants from spreading. Additionally, its biomass has multiple uses, including bioenergy production, fiber materials, and paper production, making it an economically viable crop, especially for degraded land. Organic soil amendments, like biochar and biostimulants, offer promising solutions to stimulate plant growth and yield in contaminated and degraded soil, supporting ecosystem health. Biochar, produced from biomass, enhances soil structure, retains moisture, and improves nutrient availability. Biostimulants, including microbial and organic compounds, help plants grow stronger, improve soil microbes, and increase crop yields.

Data on the impact of biochar on *M×g* yield in degraded, depleted soil are still scarce, and the findings remain inconsistent. Furthermore, the influence of biochar and biostimulants on soil nematode communities, essential for determining *M×g* crop yield in degraded or depleted soils, has received limited scientific attention and remains poorly understood [3,4].

This study examines how biochar and the biostimulant BioHelp affect soil nematodes in nutritionally poor, depleted soil in a post-military area of the Kyiv region. Given the critical role of nematodes in soil health and nutrient cycling, understanding their response to organic treatments is essential for enhancing soil restoration efforts. This research will provide valuable insights into the ecological impacts of biochar and biostimulants, contributing to the development of more effective strategies for post-military land rehabilitation and the advancement of sustainable agriculture in regions affected by military activities.

Materials and methods

A long-term phytotechnology experiment with *M×g* using the commercially produced biochar “Ideale” made from industrial wood waste in two doses (5%, 10%) and the BioHelp growth biostimulant obtained through deep cultivation of the *Azotobacter chroococcum* strain was initiated in Vorzel, Bucha district, Kyiv region, in 2023. The experimental design is represented in Figure 1.

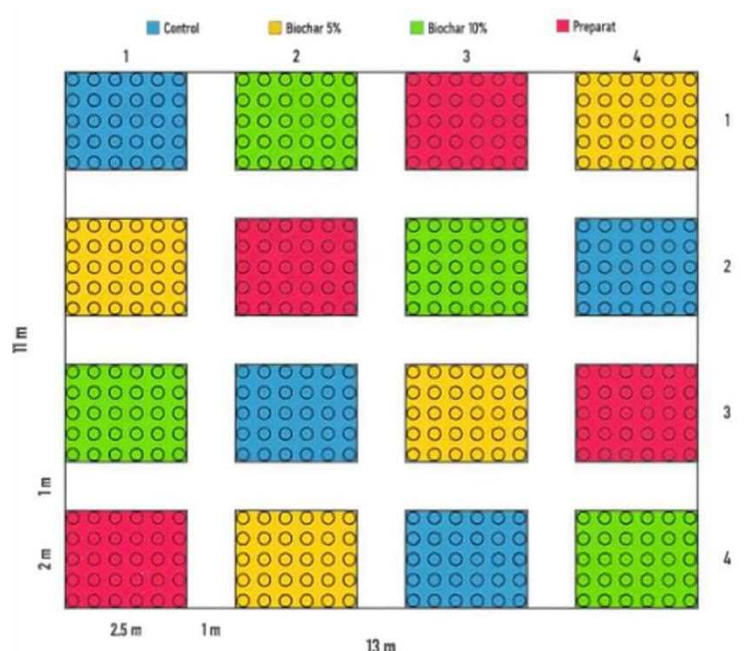


Fig 1. The schematics of the experiment set up in 2023, Vorzel, Ukraine.

Biochar was applied before planting *M×g* in 2023. The Miscanthus variety "Ossinuy zorezvit" was used for planting. Before planting, BioHelp was applied. The biostimulant was evenly spread over the soil surface in a 1 cm layer.

The agrochemical characteristics of the soil were assessed before the establishment of the plantation. The soil was identified as sandy, with weak to moderate podzolization and low humus content. The soil is characterized by low pH (4.78), NH_4^+ (30/1), and Humus Content (1.16).

Elemental analysis using X-ray fluorescence analysis of the soil was conducted twice: once before planting Miscanthus and again at the end of the first year of vegetation in 2023. The process of soil sample preparation and analytical procedures was detailed by Pidlisnyuk et al. (2018).

Nematode monitoring was provided in 2023-2024 based on three sampling times: October 2023, May, and September 2024. For nematode isolation from soil, we used a modified Baermann funnel method and the centrifugation-flotation technique [4, 5]. For the identification of plant-parasitic and free-living nematodes, identification keys were used. [7, 8]. Nematode communities were analyzed based on their total abundance and their proportion in soil samples. The soil nematodes were classified into five trophic groups [9].

At the end of the 2024 growing season (the second year of crop vegetation), the dry matter yield was assessed. The aboveground biomass of *M×g* was harvested from each experimental plot and immediately weighed to determine fresh biomass. The samples were then chopped into uniform pieces to ensure consistent drying and placed in a forced-air oven at **60–70°C** until a constant weight was achieved. To confirm complete drying, samples were periodically weighed at **24-hour intervals** until no further weight reduction was observed. The final dry weight was recorded, and the dry matter content was calculated as the ratio of dry biomass to fresh biomass.

Statistical analysis was conducted using Program Statistica by **ANOVA test**.

Results and discussions

This study assessed the concentrations of trace elements in soil samples treated with biochar and biostimulants. The trace elements detected included magnesium (Mg), aluminum (Al), chromium (Cr), manganese (Mn), nickel (Ni), copper (Cu), zinc (Zn), rubidium (Rb), strontium (Sr), and lead (Pb). The concentrations of these elements were measured across different experimental variants, and their levels were compared against the Maximum Permissible Levels (MPL) as outlined by regulatory standards.

Overall, the trace elements found in the soil were largely within acceptable limits, with some fluctuations observed for Pb and Zn. However, significant concerns arose with manganese (Mn) and copper (Cu), which exceeded the MPL. The highest recorded concentration of Mn was 259.48 mg/kg, surpassing the upper permissible limit for soils with a pH above 6.0, which is set at 100 mg/kg. Similarly, copper levels were found to be elevated, with the highest concentration reaching 9.68 mg/kg, exceeding the MPL of 3 mg/kg. Lead (Pb) concentrations also raised concern and warrant further attention, though they remained within the acceptable range.

The total of nematode communities is represented by 5 trophic groups, including 24 genera and 3 families. Soil nematode communities responded differently to the applied treatments, reflecting changes in soil health.

The nematode faunal (Fig. 2) analysis showed that the highest nematode abundance was recorded with 10% biochar treatment, while the lowest was with 5% biochar. Despite its potential positive impact, the 10% biochar treatment exhibited high variability in results. The ANOVA test indicated that treatment effects were close to statistical significance, suggesting a likely non-random influence on nematode abundance. However, the interaction between treatment and sampling time was not significant.

During the research from 2023 to 2024, significant changes in nematode abundance were observed. Consequently, this led to corresponding changes in the percentage ratio of nematodes from different trophic groups (Fig. 3). Seasonal fluctuations did not affect the total nematode abundance. The application of amendments and stimulants influenced nematode communities.

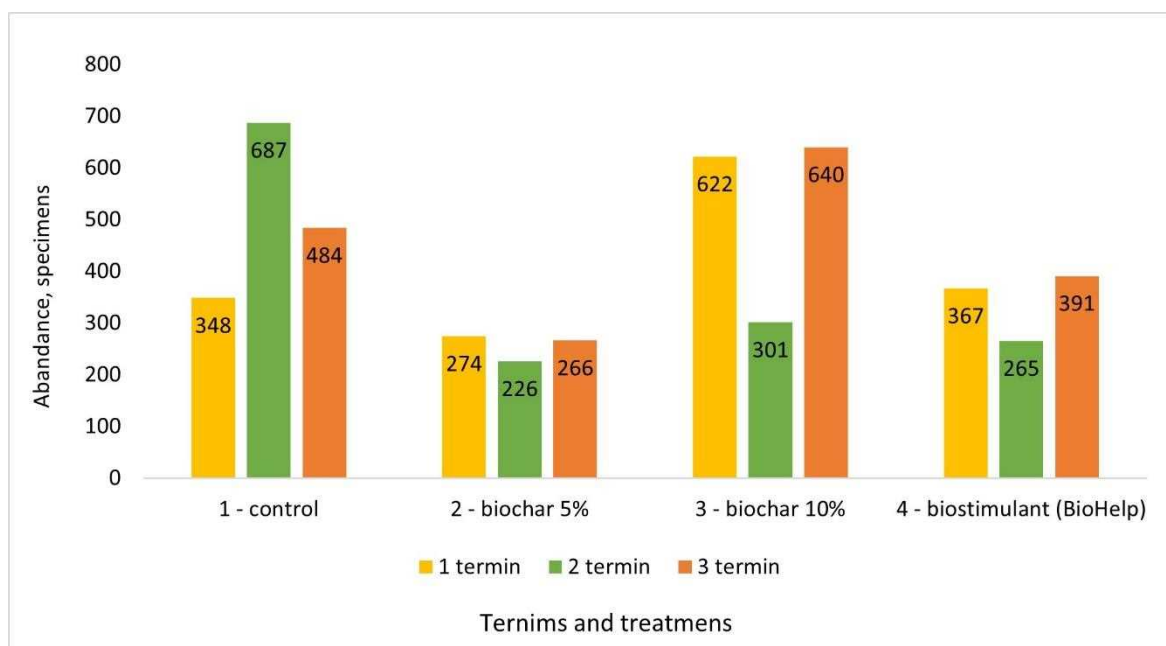


Fig. 2. Nematode abundance in response to termins and treatments and, Vorzel, Kyiv region, 2023-2024.

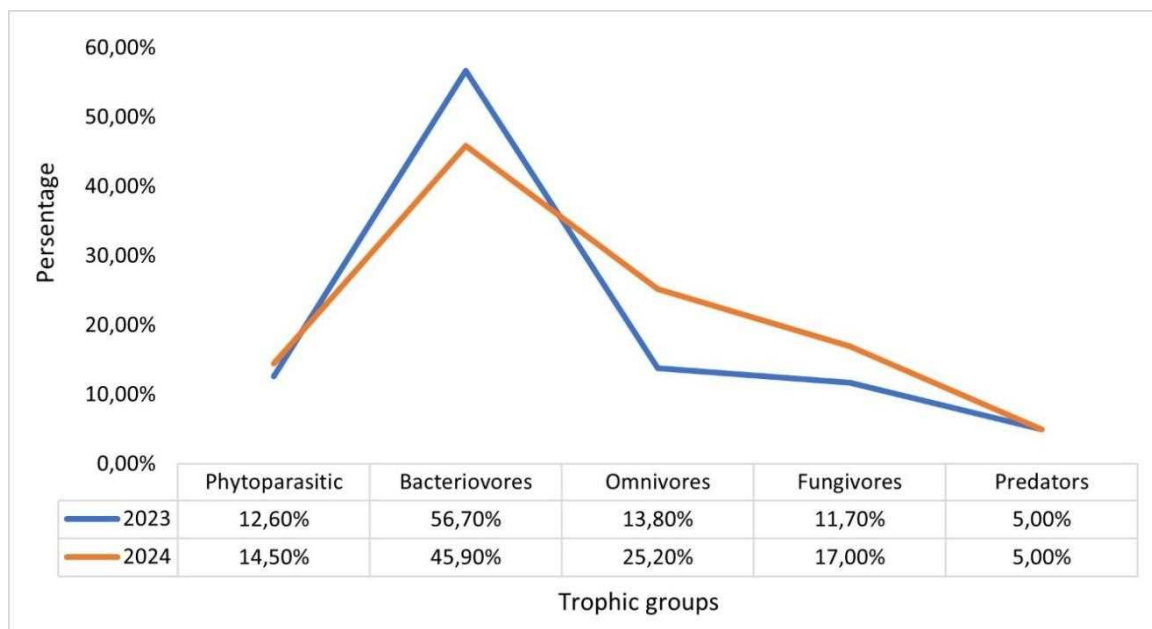


Fig. 3. Percentage of nematode trophic groups, Vorzel, Kyiv region, 2023-2024.

Under the influence of biochar, the nematode community structure shifted significantly between 2023 and 2024. The proportion of omnivores (13.8% → 25.2%) and fungivores (11.7% → 17.0%) increased, while bacteriovores declined (56.7% → 45.9%). Phytoparasitic nematodes showed a slight increase (12.6% → 14.5%), whereas predators remained stable at 5.0%, indicating a balanced predatory presence [10].

The statistical analysis of the nematode trophic groups shows a clear reduction in variability over time. In 2023, the variance was 0.0433, and in 2024, it decreased to 0.0311 and 0.0286. This decline indicates that the nematode communities have become more uniform and stable across the different experimental treatments. As the study progressed, the soil environment appeared to reach a state of equilibrium, resulting in more consistent responses from the nematode populations.

The dry weight yield of *M×g* in the second year of vegetation exhibited variations in response to biochar and biostimulant application. The yield of *M×g*, expressed as dry weight in the second year of vegetation, varied in response to biochar and biostimulant application (Fig. 4).

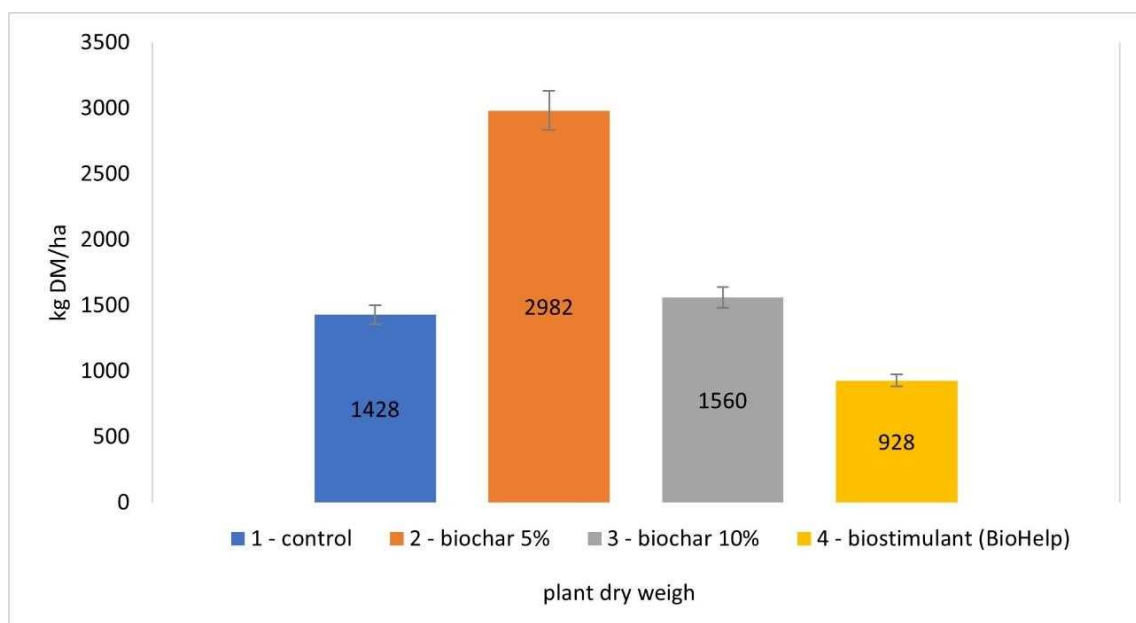


Fig 4. Effect of biochar and biostimulants on *M×g* yield, 2024 year, Vorzel, Kyiv region.

Overall, the trace elements found in the soil were largely within acceptable limits according to the MPL, with some fluctuations observed for Pb and Zn. The elevated concentrations of Mn and Cu raised significant concerns. The highest recorded concentration of Mn (259.48 mg/kg) exceeded the upper permissible limit for soils with a pH above 6.0, set at 100 mg/kg. Similarly, copper levels surpassed the MPL of 3 mg/kg, reaching 9.68 mg/kg in some treatments [12].

This is particularly concerning given that while our experiment started with acidic soils, it is well-documented that biochar can increase pH. Consequently, this pH shift may result in the soil exceeding the threshold permissible levels for certain elements, raising potential environmental and regulatory concerns. Further research is needed to explore the long-term effects of these trace elements on soil fertility and ecosystem functions.

Pb concentrations, while still within the acceptable range, warrant further attention as they showed some fluctuation. Monitoring Pb levels over time and evaluating their potential effects on soil health will be important for future studies.

Trace elements and metals were detected in the research soil. Given the deficiency of essential macro- and micronutrients in the soil environment, the presence of trace elements may further restrict nutrient availability, affecting plant cover development and biogeochemical processes in the ecosystem.

The trophic structure of the nematode communities shifted over time. The increase in the number of omnivores and fungivores, along with the decline in bacteriovores, suggests that biochar amendments may have altered microbial activity and nutrient cycling within the soil. This shift could reflect changes in soil composition and microbial communities induced by biochar and biostimulants. The slight increase in phytoparasitic nematodes could indicate some degree of soil stress or imbalance, while the stable presence of predators suggests that predator-prey relationships remained balanced in the nematode community.

The reduction in the variance of nematode trophic groups over time suggests that the nematode community structure may be stabilizing, possibly due to the long-term effects of the amendments, which could help create a more homogeneous community structure. These changes emphasize the importance of carefully monitoring amendments to prevent unintended disruptions to soil biodiversity.

In this study, biochar treatment resulted in the highest dry biomass yield (BD2). However, the lack of a proportional yield increase suggests that there may be an optimal concentration of biochar beyond which further application does not lead to additional benefits. This observation is consistent with previous studies showing that excessive biochar application can lead to nutrient imbalances or alter soil microbial communities, potentially diminishing its effectiveness [11,13,14].

In contrast, the biostimulant Biohelp resulted in the lowest productivity values, suggesting its impact on crop performance was limited compared to biochar. This could be attributed to variations in soil conditions and crop species, as biostimulants are known to have variable effects depending on these factors [15,16]. While biostimulants have been reported to enhance plant resilience and nutrient uptake, their effectiveness varies depending on soil conditions and crop species.

The results align with previous research on the potential benefits of biochar for improving soil health and crop productivity [17]. However, further investigation is needed to understand the mechanisms through which biochar and biostimulants interact with soil and plant physiology. Future studies should focus on optimizing application rates and combinations of biochar and

biostimulants to maximize benefits while minimizing potential negative effects on soil health and crop yield.

Conclusions

This study focused on the impact of biochar and biostimulant treatments on soil health, particularly in post-military degraded soils, where nutrient deficiencies and elevated trace element concentrations are of concern. Elevated levels of manganese (Mn) and copper (Cu) were detected, surpassing the Maximum Permissible Levels (MPL). Given the deficiency of essential macro- and micronutrients in such soils, the presence of these elevated trace elements may further restrict nutrient availability, potentially hindering plant growth and disrupting biogeochemical processes in the ecosystem. The nematode community was significantly influenced by biochar treatments, with notable shifts in trophic groups, particularly the increase in omnivores and fungivores. However, the high variability in nematode abundance underscores the need for further research to fully understand the long-term effects of biochar and biostimulants on such degraded soils.

Future studies should prioritize investigating the long-term impact of trace element accumulation on soil health and nematode communities, particularly in post-military soils, which may have unique environmental challenges. Understanding how elevated Mn and Cu concentrations affect nematode diversity and functionality in these degraded soils will be crucial for maintaining ecosystem balance and nutrient cycling. Additionally, research should examine the commercial yield of *Miscanthus* in these soils, assessing how the treatments influence plant productivity and ensuring sustainable agricultural practices in post-degraded military landscapes. This will provide insights into optimizing soil remediation techniques while mitigating the negative effects of trace element accumulation on crop yield and soil health.

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Methods of Initial Assessment for Safety Secondary Application of Duroplastic Waste

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Abstract. *The powder recyclate was obtained through the mechanical processing of GRP waste (pipes, wind turbine blades). Currently, there are no specific quality requirements or standards for such secondary material due to the lack of its large-scale usage. However, pending regulations dedicated to the secondary markets, it is necessary to develop facilitate the potential introduction of the material on an industrial scale. The recyclate was analyzed using gas chromatography (GC), high-performance liquid chromatography (HPLC), and Fourier-transform infrared spectroscopy (FTIR).*

Keywords: conference, conference proceedings, paper layout, paper sample, research paper secondary raw materials, application safety, circular economy, sustainability.

Introduction

Composites are materials composed of at least two distinct phases that synergistically combine their properties, exhibiting unique mechanical and physicochemical characteristics unattainable by their individual components. Fiber-reinforced resin composites are increasingly used in the aerospace, transportation, and energy industries [1].

They consist of a matrix and a filler. One of the most commonly used matrix materials is epoxy resin, which exhibits excellent electrical, thermal, and mechanical properties. However, due to its three-dimensional network of covalent bonds that cannot be easily broken, recycling epoxy resins and thermoset-based composites poses a significant challenge[2]. Over the past two decades, wind energy has developed at an exceptionally rapid pace, becoming one of the most economically viable sources of renewable energy. One of the most critical components of wind turbines is the blade, which is made of composite materials, making recycling challenging. Due to the operational lifespan of wind turbines, the first wave of early installations is now approaching the end of its life cycle. Consequently, the issue of wind turbine blade disposal is emerging as a significant concern, along with the potential negative environmental impact of thermoset waste [3]. To ensure a circular economy for plastics, it is crucial to understand the environmental impact of recycling and to make optimal recycling choices for specific materials [4]. Due to the significant amount of waste material from wind turbine blades, there is a need to develop a method for their reuse.

This article focuses on evaluating the safety of secondary filler applications, obtained through the mechanical processing of wind turbine blades — one operated in offshore conditions and the other not used at all.

The circular economy is a significant concept in many regions of the world and across various industrial sectors. Secondary application (reuse) plays a crucial role in sustainable development, influencing multiple environmental, economic, and social aspects. The importance of secondary utilization is evident in areas such as natural resource conservation, waste and pollution reduction, energy savings, and the reduction of greenhouse gas emissions.

The aim of the preliminary safety assessment of polymer powders obtained through the mechanical processing of thermoset materials is to evaluate the potential for their secondary application in combination with the primary matrix.

There are three main approaches to the recycling of GRP materials: thermal, chemical, and mechanical methods. However, due to economic and environmental considerations, this study focuses on mechanical methods for producing recyclate [5].

Sources of thermosetting waste raw material

Renewable energy is gaining increasing significance, with wind power being one of its key sources. Wind turbine blades, essential for harnessing this energy, are typically made from composite materials, most commonly consisting of glass fiber reinforced with epoxy or polyester resin [6]. These blades have an average lifespan of approximately 20 years, after which they are decommissioned and end up in landfills [7]. According to estimates by the WindEurope association, approximately 25,000 tons of wind turbine blades will reach the end of their service life by 2025. The highest number of decommissioned wind turbine blades will be recorded in Germany and Spain, followed by Denmark, and towards the end of the decade, in Italy, France, and Portugal. It is projected that the annual amount of decommissioned blades could increase to 52,000 tons by 2030 [8].

Attention should also be given to the maritime industry. Since the 1950s, glass fiber-reinforced polyester resin composites (GRP) have gradually replaced wood and metal as the primary material for constructing small recreational and work boats. These vessels often remain operational even after their expected service life, which is approximately 10 years for inflatable boats, 20 years for motorboats, and over 30 years for sailboats [9].

Over the past two decades, numerous studies have been conducted to replace glass fiber and other materials that are difficult to recycle and pose disposal challenges in composite manufacturing. The main objective of these efforts is to enhance the environmental sustainability of these materials, particularly in terms of their disposal after the end of their service life [10].

Differences in the waste source (primary application) may result in chemical composition and amount of reinforcement, presence of modifiers, environmental stability, and others.

Differences in waste source, and thus its properties, may also be visible in the case of different exploitative histories, i.e., post-exploitative waste (long-term used), production waste (not used), waste from failure state (short-term, variable usage). This may differ in the waste in chemical compounding, the amount of reinforcement, and the degradation level.

Application examples

Recycled thermosets may find circular or new applications in enhancing material properties across different industries. Recycled thermosets are used as a reinforcing additive in polyurethane foams. The resulting reinforced foam exhibits improved properties, such as enhanced sound absorption and compressive strength [11]. Additionally, recycled FRP (Fiber-Reinforced Polymers) can be utilized as a filler in asphalt [12] and as a reinforcement in cement mortar [13].

In the context of the wind energy sector, recycled end-of-life glass fiber-reinforced wind turbine blades, following appropriate modifications, can be effectively repurposed as a feedstock for the Fused Filament Fabrication (FFF) 3D printing process [14]. Moreover, the functionalization of styrene-butadiene rubber enables its chemical recycling and the creation of a closed-loop system for this material [15]. These examples highlight the growing potential of recycled thermosets in reducing waste and improving the sustainability of various industries. Further development in this area should instead be focused on a circular economy because this would allow for the closure of the loop in raw materials, lower their consumption and carbon footprint, as well as stay at the same level of economic costs since the requirements would not be changed.

Preliminary Safety Assessment Methods in the Conducted Research

The research results presented in the article concern two types of recyclates obtained from the mechanical processing of offshore wind turbine blades. One of them had been in operation for about a decade in marine atmospheric conditions (WTB – offshore), while the other had not been used in natural conditions (WTB – not used).

During the research, the focus was placed on a detailed analysis of the composition of the investigated recyclates, with particular emphasis on the presence of bisphenol A (BPA). Although this substance is considered toxic, it is a main component in the production of epoxy resins [16].

To this end, two parallel analyses were conducted. The wind turbine-based recyclates were extracted using water. The resulting solution was analyzed using gas chromatography (GC) and high-performance liquid chromatography (HPLC).

For the purposes of the planned research, two parallel analyses were conducted. It was conducted on recyclate samples, which were extracted in demineralized water for 144 hours.

The results of the analyses did not show the presence of bisphenol A in any of the prepared samples, regardless of the applied analytical method (GC or HPLC). Additionally, an analysis of the presence of amines, particularly aromatic amines, was performed based on the results obtained from gas chromatography (GC), using the library data of the software associated with the chromatograph. This analysis did not detect any amines in the tested samples.

A full scan analysis was also performed using gas chromatography (GC), encompassing recyclates in their free form (powder). Two different columns were used for this purpose: VF-624MS – for volatile organic compounds, and DB-5MS – for substances with higher molecular weight.

For the WTB – offshore recyclate, gas chromatography (GC) analysis utilizing the VF-624MS column identified the presence of 2-methoxy-2-methylpropane, n-hexane, toluene, ethylbenzene, p-xylene, styrene, 1-ethyl-3-methylbenzene, and benzyl alcohol. In contrast, the analysis of the WTB – not used recyclate revealed the presence of hexane, toluene, butyl acetate, p-xylene, styrene, and benzyl alcohol. GC analysis performed with the DB-5MS column detected ethylbenzene, p-xylene, styrene, 1-ethyl-2-methylbenzene, 1,2,4-trimethylbenzene, and benzyl alcohol in the WTB – offshore recyclate, whereas for the WTB – not used sample, only p-xylene and styrene were identified.

To determine the functional groups present in the recyclates, the samples were analyzed using Fourier Transform Infrared Spectroscopy (FTIR). The analysis of the FTIR spectrum of the powder recyclates composed from chopped composites of glass fiber and resin requires the interpretation of characteristic peaks to identify the components and functional chemical groups.

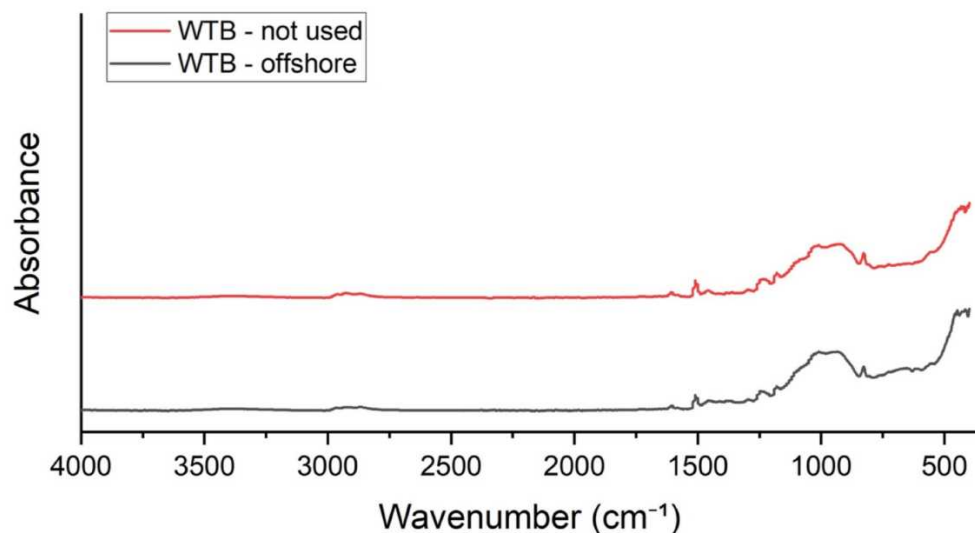


Fig. 1. FTIR spectra of the recyclates WTB – not used and WTB – offshore.

The peak observed at 2950 cm⁻¹, which is small and broad, often indicates the presence of bands associated with C-H stretching in methyl (-CH₃) and methylene (-CH₂-) groups. This peak may correspond to the resin, particularly the aliphatic fragments present in the polymer matrix.

The peak observed at 1510 cm⁻¹ is often attributed to deformation bands of C=C bonds in aromatic rings. This suggests the presence of aromatic components in the resin, particularly those associated with epoxy resins. Aromatic structures are characteristic of epoxy composites, as compounds like bisphenol A serve as key precursors in their synthesis.

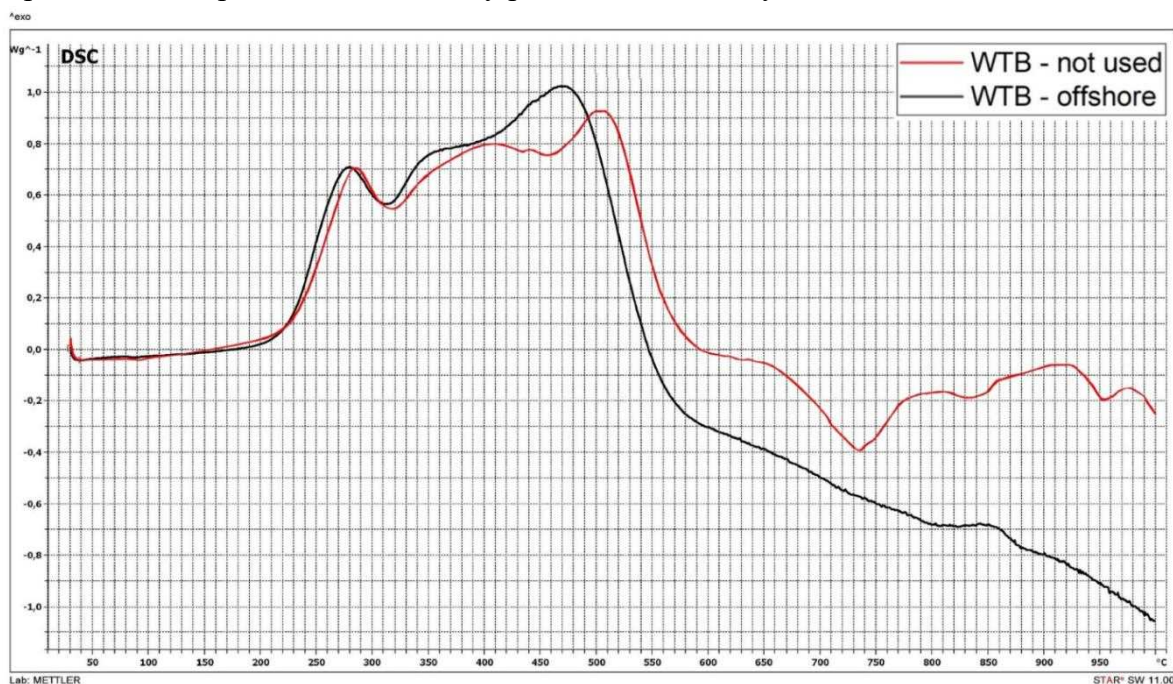


Fig. 2. DSC thermogram of recyclate WTB – not used and WTB – offshore.

Heating rate of 5°C/min.

Recyclate WTB - offshore and WTB – not used were subjected to thermal analysis. In Fig. 2 - 3, the thermograms of Differential Scanning Calorimetry (DSC) and Thermogravimetric Analysis (TGA) are presented.

By analyzing the TGA curve of WTB - offshore, it is possible to determine the chemical composition, including both quantitative and qualitative analysis of the tested sample. The organic fraction, i.e., the resin with the hardener, constitutes 26 wt%, while the remaining 74 wt% consists of mineral reinforcement.

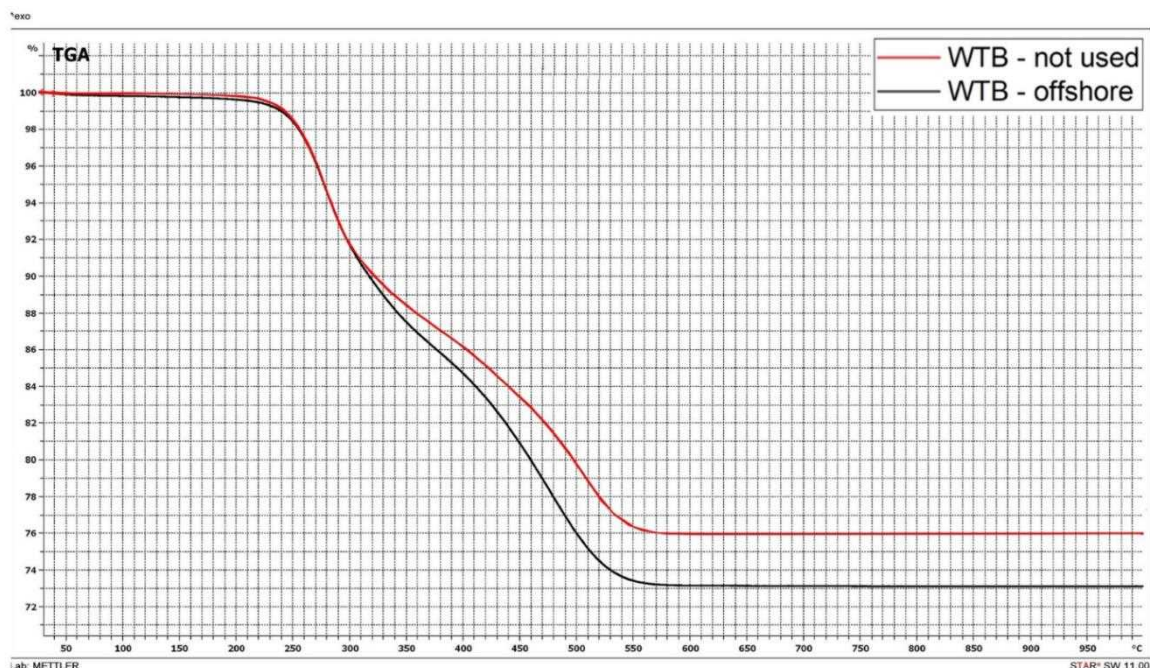


Fig. 3. TGA thermogram of recyclate WTB – not used and WTB – offshore.
Heating rate of 5°C/min.

A slight, negligible moisture content in the recyclate is observed (a small mass loss recorded below 100°C). The material decomposition occurs in two stages (which indicates that the composite body consists of epoxy resin cured with an acid anhydride) within the temperature range of 250°C to 580°C.

By analyzing the TGA curve of WTB – not used recyclate, it is possible to determine the chemical composition, including both quantitative and qualitative analysis of the tested sample. The average organic fraction, i.e., the resin with the hardener, constitutes 25 wt%, while the remaining 75 wt% consists of mineral reinforcement.

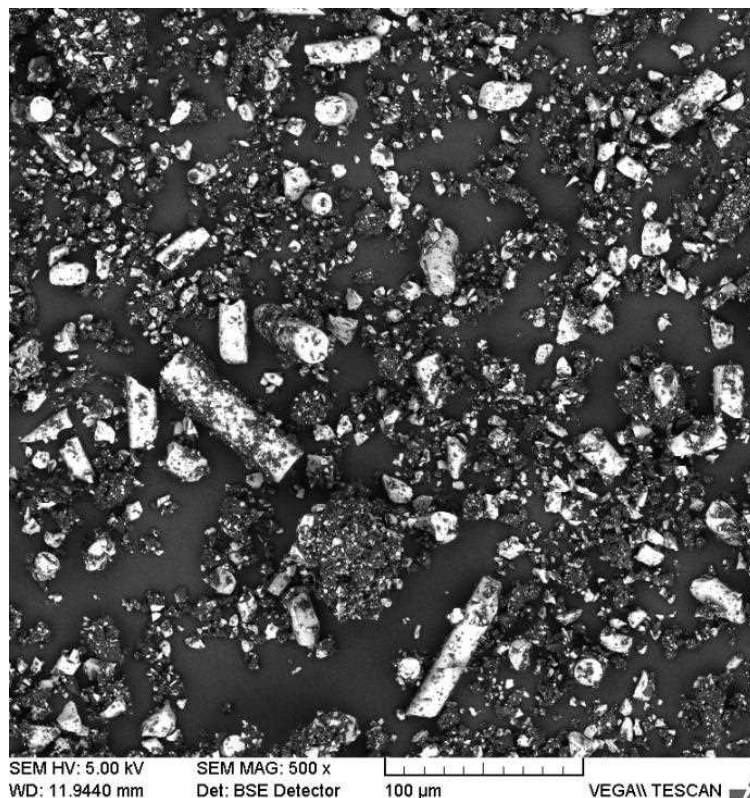


Fig. 4. SEM image of the WTB - offshore at 500× magnification.

A slight, negligible moisture content in the recycle is observed (a small mass loss recorded below 100°C). The material decomposition occurs in two stages (which indicates that the composite body consists of epoxy resin cured with an acid anhydride) within the temperature range of 150°C to 580°C.

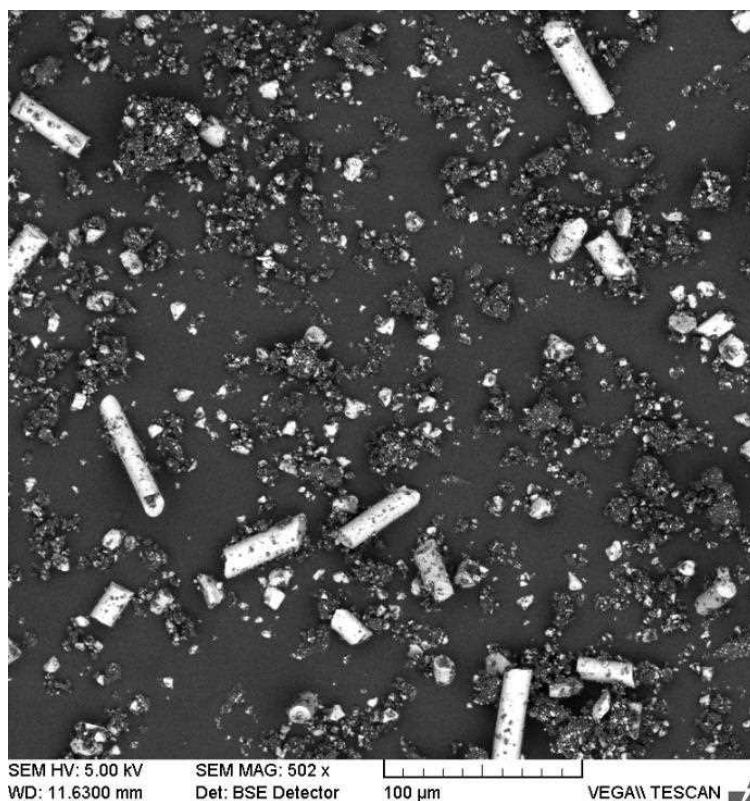


Fig. 5. SEM image of the WTB – not used at 500× magnification.

The presented microscopic images were taken at a magnification of 500x. The images reveal recycle grains with diameters not exceeding 50 μm. The presence of agglomerates, formed by the fusion of smaller grains, is also observed. Individual recycle grains exhibit an irregular shape with sharp edges.

Microscopic images of the recycle from WTB – offshore show the presence of glass fiber fragments with lengths below 100 μm and organic resin particles with diameters smaller than 50 μm. The observed fibers are also characterized by the presence of fine recycle fractions on their surface.

The recycle from WTB – not used is characterized by the presence of glass fibers and resin fractions. Some individual fibers with lengths of approximately 200 μm can be observed; however, the vast majority of fibers are shorter than 100 μm. The observed fibers are largely covered with fine fractions of organic resin.

Conclusions

Recycled thermosets have already found various applications in enhancing material properties across different industries and should be further developed, where the circular application is very perspective. The initial tests show that regardless of the exploitative history and the compound used, blade waste and recycles of blade waste don't contain VOCs, and their heat resistance and chemical structure are safe and similar enough to use this waste as a regular secondary material.

The detailed analysis of recycle samples, including those derived from wind turbine blades - operated at sea and not- did not reveal the presence of bisphenol A (BPA) or amines, particularly

aromatic amines, across all extraction methods and analytical techniques used. Despite the recognized toxicity of BPA and its role in the production of epoxy resins, no traces of this compound were detected in any of the samples analyzed using gas chromatography (GC) or high-performance liquid chromatography (HPLC).

The absence of BPA is a significant finding, indicating that either the recycling processes involved did not release or retain BPA, or that the levels of BPA were too low to be detected by the chosen analytical methods. This is important from both an environmental and health perspective, as BPA is a substance of concern.

Additionally, a thorough gas chromatography analysis revealed the presence of various other organic compounds, such as styrene, toluene, ethylbenzene, p-xylene, and benzyl alcohol, across the different recycle samples. The presence of these substances could be indicative of residual chemicals from the production and processing of the original materials or potential by-products formed during recycling. While none of these compounds posed an immediate concern in terms of toxicity, their identification may warrant further investigation into their sources and potential implications for the recycling process.

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State Policy in the Field of Ecologization Trade-Logistics Centers

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Abstract. *The article examines state policy in ecologizing trade-logistics centers, focusing on environmental impact reduction through regulations and sustainable logistics strategies in Ukraine. It highlights financial mechanisms like tax incentives and grants, international experiences, Ukrainian companies adopting environmental standards, and NGO influence on policy. It emphasizes the need for comprehensive ecologization approaches integrating regulation and financial incentives.*

Keywords: ecologization, state policy, logistics, trade-logistics centers.

Introduction

The formation of environmental policy is a process that belongs to the highest levels of policy. The most important aspect is the implementation of environmental policy at the micro level, within each enterprise and facility that affects the state of the natural environment. Environmental policy must include premises such as a healthy population cannot exist in an unhealthy natural environment, environmental issues cannot be resolved at the expense of economic development or beyond its limits, and reducing environmental damage is a necessary condition for economic development [1].

According to the Law of Ukraine "On Environmental Protection," compliance with environmental regulations is mandatory, indicating their particular significance for environmental protection [2].

The Sustainable Logistics Strategy for Ukraine for the period up to 2030 is a systemic national document on the logistics-production potential of the country. The document reflects the concept of satisfying population needs in transportation. The strategy aims to enhance logistics efficiency in economic, social, environmental, transportation, and production spheres, as well as their sustainability. Environmental sustainability includes minimizing external impacts, particularly emissions affecting the natural environment and people during the operation of transport and production systems [3].

Results and discussion

According to Article 30.1 of the Tax Code of Ukraine, tax relief refers to exemptions provided by tax and customs legislation from the obligation to accrue and pay tax or the payment of tax and duty in a smaller amount under conditions provided by legislation. Tax incentives have a dual nature, and it is necessary to determine their advantages and disadvantages. On the one hand, they stimulate enterprises to operate in certain areas, while on the other hand, they create conditions for the emergence of tax minimization or evasion schemes. Another significant issue of the tax relief system is the complexity of objectively monitoring the benefits and the effectiveness and expediency thereof in certain sectors of the economy as a whole [4].

In addition to environmental taxes and tax incentives to support the development of green technologies, subsidies and grants should also be considered, such as for the construction of solar power plants [5]. Lithuanian transport and logistics companies apply "green logistics" practices motivated by subsidies and incentives [6]. Also relevant is the formation of a financial mechanism for project implementation under government guarantees with reduced bank loan interest rates [7].

A good example is "green" financing implemented in China, which effectively supports the modernization of industrial infrastructure through the introduction of "green" loans and "green" bonds. Ukraine has also implemented a similar approach; for example, in 2019-2021, the first issuances of green bonds took place. In 2019, DTEK issued bonds on the Irish Stock Exchange with a circulation period of 5 years and an 8.5% annual interest rate for the construction needs of the Tyligulska SES, and in 2021, UkrEnergo issued "green" bonds on the London Stock Exchange also with a circulation period of 5 years at a 6.75% annual rate. The issuance of "green" government bonds did not take place due to martial law, and the issuance of domestic government bonds and local government bonds [8].

To assess the effectiveness of innovation-investment projects, it is necessary to use a synergistic eco-economic effect from their implementation, which takes into account both ecological, economic, and social aspects of the projects [9].

A notable example of positive shifts in the ecologization of the logistics sector is the companies "ZAMMLER UKRAINE" and "ZAMMLER SKLAD," which received ISO 14000 certification in 2017. Among the criteria for assessing the environmental performance of companies are tire recycling, sorting of packaging waste, and its utilization. In addition, companies are considering the application of "eco-driving" technology, aiming to achieve fuel savings through the high professional training of drivers, thereby applying modern technologies to control harmful emissions [10].

Another vivid example of innovative technology implementation is the company "SILPO-FOOD." In 2021, the company created the first robotic warehouse zone in Ukraine, where 31 AGV robots of the Geekplus RS-2 type perform product movements within the warehouse. The autonomous mode of operation of such robots reaches up to 12 hours, and labor productivity has increased 2-3 times, while ensuring error-free operations at 99%. The company also continually modernizes its fleet, adhering to "Euro-5" and "Euro-6" environmental standards. The use of the Webfleet GPS system reduces adverse environmental impacts by optimizing routes and saving fuel and lubricants [11].

Addressing environmental issues in Ukraine's logistics system, several environmental benchmarks are evident in the National Transport Strategy of Ukraine up to 2030, which aims to ensure socially safe, environmentally friendly, and energy-efficient transport [12].

Non-governmental organizations are typically established by local communities that understand local problems and needs well and have connections with all community representatives, which is important for determining the goals of voluntary social activities. These include public and charitable organizations, charitable foundations, and credit unions formed by the voluntary participation of citizens. Statistics show that the main sources of funding for NGOs are divided into such revenues as contributions from non-residents - 33%; enterprises and organizations of Ukraine - 15%; economic activities of legal entities created by the organization itself to achieve its goals - 15%; membership fees - 10%; citizens of Ukraine - 5%; the State Budget of Ukraine - 3%; and 16% accounted for other sources [13].

The primary area of activity of non-governmental organizations is environmental conservation. They play a crucial role in advocating biodiversity conservation policies, promoting sustainable development, and mitigating the effects of climate change. By conducting research and implementing various projects at the community level, they aim to address environmental issues. By working together on common issues, NGOs build trust, dialogue, and cooperation among states and participants in regional conditions [14].

The activities of such organizations stimulate enterprises to implement environmental practices for waste reduction and recycling, and also contribute to increasing environmental responsibility. Additionally, they can collaborate with the private sector to develop and implement environmental programs, such as creating environmental education projects or funding environmental initiatives.

The goal of environmental projects is to address specific environmental issues through changes in the state of the natural environment. The main risk of project implementation is reduced funding, which requires adjusting measures, as well as a possible lack of inter-project coordination, limiting the ability to apply experience gained in implementing related projects.

UN environmental policy stipulates that 2% of the world's GDP should be invested in environmental transformation of the economy to reduce emissions into the natural environment and efficiently use resources [15].

Ukraine is a party to a significant number of international agreements in the field of environmental protection, and cooperation between Ukraine and the EU since 1998 has aimed at combating environmental deterioration. The agreement provides for effective monitoring of pollution, combating air and water pollution, and restoring the natural environment [16]. Integrating the environmental component is one of the key tasks of Ukraine's "green growth" - introducing effective measures and new principles for integrating the environmental component into all sectors of the economy, and cooperation between Ukraine and the EU plays a crucial role in reforming, developing environmental legislation, and transforming nature conservation institutions [17].

The EU supports Ukraine's development in the field of environmental protection and helps adapt legislation to EU requirements [18]. Examples of EU projects and grants in Ukraine are presented in Table 1:

Table 1

European Projects in the Field of Environmental Greening in Ukraine

Name	Task	Date	Budget
Covenant of Mayors – Demonstration Projects	Reduction of carbon dioxide emissions by 20%	2014	€14 million
Support for Ukraine in the Approximation of EU Environmental Legislation	Strengthening the legal framework in areas such as transparent decision-making, water resource management, environmental protection, and supporting the process of aligning Ukraine's legislation with EU environmental law	2015	€2.6 million
Support for Nature Reserves in Ukraine	Construction of infrastructure in protected areas, biodiversity conservation, and development of a management system	2016	€14 million

Examples of major environmental programs in Europe include the LIFE program, which essentially serves as a financial instrument for environmental protection, promoting the development and renewal of environmental policies. Another example is the NER 300 program, the world's largest funding initiative for innovative low-carbon energy projects.

EU policy also includes the imposition of an environmental tax on the use of substances whose negative impact on the environment has been proven. Revenue from such taxes accounts

for about 3% of the total GDP and approximately 7% of total tax revenues. Additionally, revenue generated from the sale of permits within the EU Emissions Trading System in 2014 amounted to approximately €1 billion.

European legislation defines the concept of "eco-innovation" as innovations that contribute to a greener economy by reducing environmental impact and using resources more efficiently. It is important to understand the specifics of eco-innovative enterprises: they specialize in particular sectors, which facilitates the effective implementation of innovations and further development. Meanwhile, "eco-adopters" utilize the developments of other enterprises, promoting the exchange of environmental technologies.

Under the European Green Deal, aimed at achieving climate neutrality by 2050, various companies are working on implementing different projects. One example of such an initiative is the commencement of hydrogen truck testing in 2020. According to estimates by Daimler Trucks, several more years are needed before the full-scale deployment of hydrogen-powered trucks. Moreover, Italy and Japan plan to develop hydrogen engine technology for ships by the end of 2025.

Effective environmental policy is key to the sustainable development of the economy and trade-logistics centers in particular. To minimize environmental impact, state policies must consider environmental, social, and economic aspects. As an active participant in the international arena, Ukraine has the opportunity to both adopt international experience and improve its regulatory framework in accordance with global standards. It is crucial to implement these standards at all levels, from local to national and even global.

International practice demonstrates that effective instruments are not limited to taxes, fines, or emission permits; tax benefits, subsidies, and grants are also powerful tools. Applying these instruments in Ukraine will encourage enterprises, particularly trade-logistics centers, to adopt green technologies and take responsible measures to protect the environment from harmful impacts.

Conclusions

State policy on the ecologization of trade-logistics centers is vital for Ukraine's sustainable development. Implementing environmental standards and financial support mechanisms (tax incentives, subsidies, grants) helps reduce environmental harm.

International experience shows the need for a comprehensive approach combining regulation, incentives, and NGO involvement. Ukrainian companies already demonstrate progress through ISO 14000 certification, eco-driving technologies, and warehouse automation.

Aligning legislation with EU standards, financing green projects, and fostering cooperation between the state, businesses, and civil society are key steps toward creating an energy-efficient and environmentally responsible logistics system.

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On Techno-Economic Analysis of Rapid Filtration of Groundwater with High Iron Content

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Abstract. *As a result of the optimization procedure at variation of composition and degree of initial contamination, a set of bed height values is determined at which the reduced costs for equipment and operation are minimized. The critical concentration and service life of the bed at increased contamination are established.*

Keywords: water treatment, iron removal, filtration, bed height, service life, technological modeling, applied optimization.

Introduction

Physico-chemical iron removal from groundwater and wastewater on rapid filters is accompanied by the formation of a deposit, which has an abnormal capability for such artificial formations to consolidate. As a consequence, the strength of the deposit increases over time, and inevitably, the amount of the deposit gradually increases in a sequence of filter runs. With the progressive clogging of the pore space, the share of its non-washable component and, commensurately, the hydraulic resistance of the operating medium and mechanical energy expenditure to overcome it increase faster [1,2]. Related nonlinear effects are especially clear at initial high iron content.

More than 50% of deep groundwater in Ukraine contains iron in amounts that are hazardous to human health. At the same time, its initial content varies significantly in the regions of the country – from 1 mg/l up to 20 mg/l. Often in rural areas, where water from head horizons can be used exclusively for drinking needs, the situation with the water supply of the population and economy is critical due to the especially high concentration of iron 3...5 mg/l. In such cases, high rates of filter contamination lead to extremely undesirable consequences, namely, the reduction of filter run duration and filter media service life, premature failure of equipment at existing iron removal facilities [3,4]. Thus, the capital and operating costs increase, low-capacity facilities have to be reconstructed, and, as a result, the efficiency of water treatment decreases.

Materials and methods

In practice, it is possible to significantly reduce the cost of water treatment by extending the mentioned period, using means of automatic control over the technological process. It is realistic to achieve this by improving the design of filters and the iron removal technology implemented on them. It is possible to substantiate such improvements under specific conditions, only involving methods of mathematical modeling. On the basis of the conceptual and mathematical models [5,6], a method for calculating spatial and temporal changes in physical and chemical conditions in the operating layer has been developed, which allows for the reliable prediction of the behavior of the most important characteristics of filtration at arbitrary initial water contamination. Previously, this method was successfully used to study the effectiveness of various control algorithms of the filter for iron removal, to develop recommendations for the rational choice of the most important design parameter, but at moderate contamination of the treated water [7]. However, the greatest

difficulties just arise in the treatment of water with increased concentration of iron. It is then the design without proper scientific substantiation can lead to emergency situations up to complete incapacity of new and reconstructed filters.

Results and discussion

Technological and design modeling of rapid filtration of natural and waste water with excessive iron content is advisable to be preceded by the establishment of the critical values of initial parameters. The physical meaning of such critical values is that they correspond to a special, boundary mode of operation of the rapid filter. At the implementation of such a mode, the liquid phase (contaminated water) will be in the filter media for a rigorously defined time (t_{cr}), during which the initial concentration C_0 will decrease to the normative value at the outlet C_* . The critical time t_{cr} can actually be interpreted as a relation $(L/V)_{cr}$ where L is the filter media height [m], V is the filtration rate [m/s]. Hence it follows that depending on specific conditions the reference value L_{cr} at the design analysis is determined as a product Vt_{cr} at a given filtration rate V , and at technological analysis already V_{cr} is calculated as a ratio L/t_{cr} at a given height L . For a strict definition of t_{cr} in general case, i.e. at the presence initially in contaminated water of two forms of iron, and in an operating layer of adsorbed oxide, deposited hydroxide, it is offered to solve the following equation by fitting

$$\frac{n_0 C_0 K_d S_a^0}{S_{mh}} \left[\frac{1}{k_a (S_{ma} - S_a^0)} - \frac{1}{k_h (S_{mh} - S_h^0)} \right] + \left[C_{a0} - \frac{n_0 C_0 K_d S_a^0}{k_a S_{mh} (S_{ma} - S_a^0)} \right] e^{k_a (S_{ma} - S_a^0) t_{cr}} + \left[C_{h0} + \frac{n_0 C_0 K_d S_a^0}{k_a S_{mh} (S_{ma} - S_a^0)} \right] e^{k_h (S_{mh} - S_h^0) t_{cr}} = C_* \quad (1)$$

Here n_0 is the clean bed porosity; C_0 is the initial volumetric concentrations of total iron; K_d is the oxidation rate coefficient of adsorbed oxide; S_a^0, S_h^0 are the inlet concentration of adsorbed ferrous iron and concentration of deposited hydroxide particles; S_{ma}, S_{mh} are the adsorption capacity of the filter medium in relation to ions Fe^{2+} and adsorption capacity of the filter media relative to the particles indicated before; k_a is the reduced adsorption rate coefficient for Fe^{2+} ; k_h is the reduced rate coefficient of hydroxide particles; C_{a0}, C_{h0} are the inlet concentrations of dissolved ferrous iron and concentrations of suspended hydroxide particles.

If deep groundwater is not aerated beforehand and it is possible to avoid contact with atmospheric air when feeding groundwater to the filter ($C_{h0} = 0$), the calculation expressions and procedure are considerably simplified. Then the formula for t_{cr} follows from Eq. (1)

$$t_{cr} = \frac{1}{k_a (S_{mh} - S_h^0)} \ln \frac{k_a S_{mh} (S_{ma} - S_a^0) C_* + n_0 K_d S_a^0 C_0}{C_0 [k_a S_{mh} (S_{ma} - S_a^0) + n_0 K_d S_a^0]} \quad (2)$$

In view of the pronounced nonlinear effects, it is of interest to theoretically study the intensification of iron removal from water with concentrated contamination by its preliminary dilution with the purified water. In such cases it makes sense to pre-calculate the critical value C_{cr} at fixed V, L . Then also Eq. (1) should be used. However, now we choose such a value of C_0

(actually C_{cr}), at which the above equation is met at the given $t_{cr} = L/V$. In the above-mentioned special case, the following expression for C_{cr} is obtained after reversing Eq. (2)

$$C_{cr} = C_0(t_{cr}) = \frac{k_a S_{mh} (S_{ma} - S_a^0)}{n_0 K_d S_a^0 + [k_a S_{mh} (S_{ma} - S_a^0) - n_0 K_d S_a^0] e^{k_a (S_{ma} - S_a^0) t_{cr}}} \quad (3)$$

However, in order to maximize the performance of the designed iron removal filter, it is necessary to resort to an applied optimization procedure. Such a procedure can be performed only on the basis of a suitable analytical solution in one or several stages, depending on the number of parameters to be optimized. Its essence is to establish by means of rationally conducted multivariate calculations such values of the sought parameters, at which the reduced costs for the arrangement and execution of the technological process would be minimal. The relevant formalisms and comments are contained in [7]. Based on them, a quantitative analysis of the operation of a typical filter for iron removal during the entire service life of one change of filtering material was carried out. At the same time, hundreds and thousands of filter runs could fit into the specified period depending on the conditions of filtration, and effective purification could last for several years. Although earlier the consequences of implementation of different filter control algorithms were studied in detail, here preference was given to the regular algorithm with a constant duration of filter runs (t_{f0}), as it does not require additional costs for automation of the technological process. At the same time from a large body of data obtained on the basis of technoeconomic calculations those of them were selected and presented in the form of illustrations, which clearly demonstrate significant difficulties arising in the practice of iron removal of heavily contaminated groundwater. The initial information for modeling was obtained earlier by processing the results of the experimental research under laboratory and industrial conditions with the use of the exact analytical solution of the basic mathematical problem [8,9].

First of all, we analyzed the effect of the degree of contamination of the water supplied to the filter (C_0) on the service life of the packed bed T_f . It was assumed that initially there are equally present divalent and trivalent iron ($C_{a0} = C_{h0} = 0.5C_0$) in the water, porous medium is clean ($S_a^0 = S_h^0 = 0$); fixed duration of filter runs (regular algorithm) discretely varied ($t_{f0} = 8, 12, 24$ hours), that allowed all the information obtained here to present in the form of a series of curves of the dependence $T_f(C_0)$ (Fig. 1).

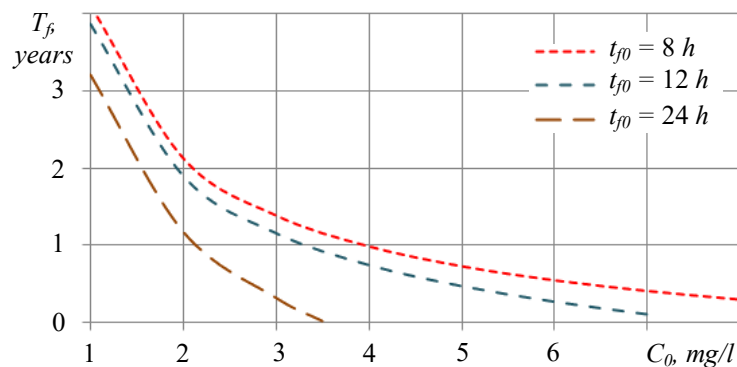


Fig.1. Dependence $T_f(C_0)$.

Their descending nature indicates the significant influence of the initial amount of impurity on the performance of the filtering material and filter facility. As the hypothetical increase in C_0 ,

the quantity T_f decreases all the way down to 0. The minimum value of T_f from the practical point of view corresponds to the critical value C_{cr} , which in general case is relatively simple to calculate by fitting from Eq. (1). In this case it is necessary to assume $t_{cr} = t_{f0}$. In a special case $C_{h0} = 0$, the value of C_{cr} is elementary calculated by Eq. (2). It is natural that the calculated curves decrease more smoothly with increasing duration t_{f0} .

In fact, it is capital costs that are closely related to the quantity T_f . A more complete pattern in economic terms can be obtained by multiple calculations of the reduced costs. Thus, it is possible to estimate the negative effect associated with C_0 for the economics of water treatment in general. The corresponding calculation data are presented in Figs. 2 and 3. First of all, the sensitivity of the costs RC was analyzed with respect to a key design parameter. Indeed, it is quite feasible to equip the filter with any reasonably bed height as opposed to the size of its elements. The importance of a careful approach to the choice of the quantity L exactly at the increased concentration C_0 is precisely indicated by Fig. 2. Firstly, even a minimal underestimation of L (deviation from the optimum L_{opt} in the direction of smaller values of L) can cause complete failure of the filter ($RC \rightarrow \infty$). Secondly, the indicated costs increase at an accelerated rate when the deviation of L from L_{opt} is upward, and this behavior of the calculated curves is particularly clear just at large values of C_0 (curve 3). In such situations it is especially important to choose L reasonably.

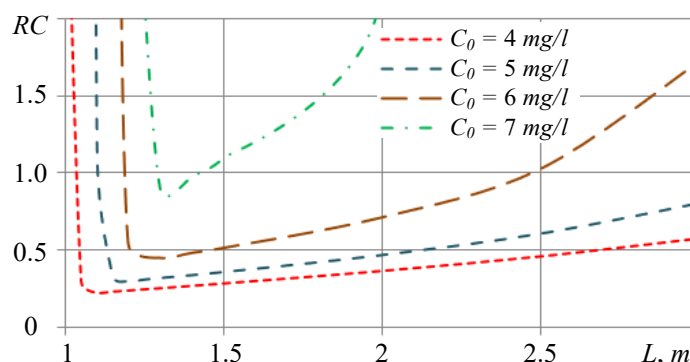


Fig. 2. Dependence $RC(L)$.

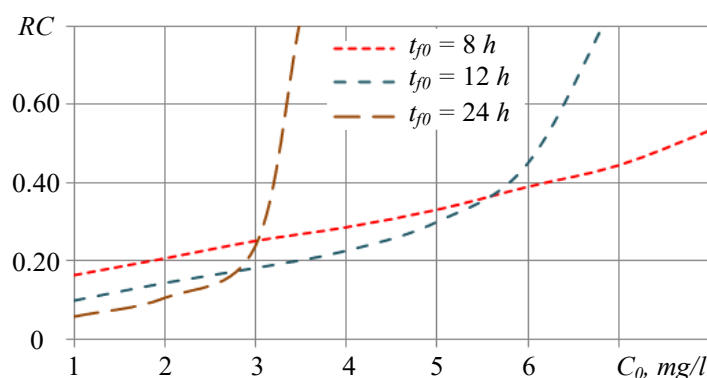


Fig. 3. Dependence $RC(C_0)$.

In the last series of calculations the value $L = 1.5\text{ m}$ is fixed according to Fig. 2. On the basis of their data, Fig. 3 shows the curves of the dependence $RC(C_0)$ at discretely varying duration t_{f0} . Hence, a close relationship between RC and C_0 is evident as in the case of the first series of

calculations. Special attention should be paid to the asymptotic behavior of the calculated curves at $C_0 \rightarrow C_{cr}$. The position of the vertical asymptote ($C_0 = C_{cr}$) is determined, as in Fig. 1, from equation (1) (at $C_{h0} = 0$ according to Eq. (3)). However, the value of t_{cr} is calculated preliminarily as the ratio of the given values of L and V .

Conclusions

In general, the results of calculations of the main economic indicators of iron removal clearly confirm the need for a reliable theoretical substantiation of the technological and design parameters in the treatment of deep groundwater with high iron content on rapid filters.

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The XPS-Revealed Difference in the Molecular Sorption Mechanism of Se(IV) and Se(VI) on Mg-Al-CO₃ Layered Double Hydroxides (LDHs) Focusing on the Material Surface Speciation

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Abstract. *This paper extends the previous work on the EXAFS-derived mechanism of Se(IV)/Se(VI) adsorption on Mg-Al-CO₃ LDHs synthesized by the original method and uses XPS surface analysis to determine the material phases responsible for the removal of these anions. A new methodological idea is suggested for distinguishing chemisorption and physisorption by XPS.*

Keywords: X-ray photoelectron spectroscopy (XPS), Mg-Al-CO₃ Layered double hydroxides (LDHs), selenate, selenite, chemisorption, physisorption, surface speciation.

Introduction

Selenium is known for its dual properties. It is one of the most important nutrients in the human body, responsible for its immune function. On the other hand, high concentrations of selenium species can be very harmful. Notably, the difference in the concentrations causing selenium deficiency problems and its high-dose toxicity is pretty narrow. In addition, over the last decade, the application of Se compounds in high technologies (catalysis, medicine, etc.) has been growing. This requires very selective materials and technologies either to strictly control its contents in water solutions or to extract it for further reuse. The knowledge-based material, Mg-Al-CO₃ Layered double hydroxides (LDHs), prepared by the discovered, purely inorganic, synthesis with a step of sol-gel routes [1], demonstrated very competitive or unique removal potential of both selenium species, selenate (SeO₄²⁻) and selenite (HSeO₃⁻). The uptake capacity obtained from sorption isotherms ranged 50-90 and 100-160 mg/g_{dw} for Se(VI) and Se(IV), respectively [2], which was one of the highest performances worldwide, according to the literature [2]. Such outstanding removal of Se anions encouraged us to investigate the molecular sorption mechanism of the aqueous selenium species on this layered material, purposefully synthesized for adsorption of toxic anions, first of all, those of tetrahedral geometry (like SeO₄²⁻, H₂AsO₄⁻). The previous study based on EXAFS-simulation discovered the difference in adsorption mechanism of Se(IV)-vs-Se(VI) on this material, and for the first time, demonstrated that selenate is unable for chemisorptive binding on this highly hydrated Mg-Al-oxide-based anion exchanger, while selenite was attracted to the same sample via (inner-sphere complexation) bidentate binuclear coordination [2]. The present work extends the previous (EXAFS-derived) data, focusing on the binding mechanism of Se species to determine the phases on the Mg-Al LDHs surface, responsible for the removal of each of these anions, selenite (HSeO₃⁻) and selenate (SeO₄²⁻) [3,4].

So, the tasks of this study were to: (1) reveal the phases of Mg and Al oxides {responsible for adsorption of Se(VI) and Se(IV)} on the surface of Mg-Al LDHs (prepared by the original method), by detailed analysis of XPS spectra of all chemical elements of the material samples, collected before and after adsorption experiments; (2) define the influence of the competing anion {sulfate (SO₄²⁻)} on adsorption mechanism of selenate and selenite at various pH values (4.5; 7.0; and 8.5); (3) compare the molecular sorption mechanism of HSeO₃⁻ and SeO₄²⁻ to determine a degree of involvement of the interlayer carbonate in their removal as a function of the competing sulfate anions and the pH values.

Materials and Methods

The material (adsorbent) used in this study was a sample of Mg-Al-CO₃ LDHs prepared by the discovered synthetic method, the fine inorganic synthesis with a step of alkoxide-free sol-gel routes [1]. The novel synthetic strategy was successfully developed to produce this layered material specifically for the application as an anion exchanger for the removal of tetrahedral anionic species (arsenate, selenate, phosphate anions) from water solutions. A detailed description of the material preparation method is shown in the previous work [1].

X-ray photoelectron spectroscopy (XPS) (also called XPS surface analysis) is a very powerful technique to investigate molecular sorption mechanisms on the surface of solid materials, which reflects the resulting interaction of adsorbent and aqueous solution (adsorbate) at the speciation level. The XPS is especially informative if combined with the other spectroscopic tools, such as EXAFS and FTIR. The XPS spectra were recorded on a Thermo Scientific K-alpha XPS system (Thermo Fisher Scientific, UK) equipped with a micro-focused, monochromatic Al K X-ray source (1486.68 eV). The digital acquisition and the data processing were carried out using the Thermo Scientific advantage software, version 5.9931 (Thermo Fisher Scientific).

Standard batch adsorption experiments, carried out until adsorption equilibrium, were applied to collect the samples for XPS spectroscopic analysis under the following experimental conditions: 2 g/L of adsorbent dose; high enough initial concentration of Se aqueous anions (450-470 mg[Se]/L) to reach full saturation of sorption sites, and the pH= 4.5; 7.0 and 8.5. The samples of Mg-Al LDHs used for these sorption experiments were filtered, washed, dried, and analyzed by XPS in comparison with the initial (not used in the sorption study) material sample. Concentrations of Se (also Mg and Al) in water solutions were measured using inductively coupled plasma optical emission spectrometry (ICP-OES) with radial plasma (CIROSCCD, Spectro A.I., Germany).

Results and Discussion

Adsorption of selenate (SeO₄²⁻). First of all, it is worth to emphasize that both tetrahedral anions, selenate (SeO₄²⁻) and competing sulfate (SO₄²⁻) (the background electrolyte added in the typical concentration levels) are attracted to the sample of Mg-Al-CO₃ LDHs via physisorption mechanism as shown in the previous article based on EXAFS simulation [2]. This means that we expected a strong competition between these two anions, resulting in a considerable lowering of the selenate adsorption on this material. However, our results showed quite a different outcome [3].

The competing aqueous sulfate (SO₄²⁻) did not greatly influence (or, at the pH=4.5, not at all) the removal of selenate (SeO₄²⁻) by the developed Mg-Al LDHs, however, it altered the adsorption mechanism, and the degree of its influence was a function of pH and the presence(A-series)/absence(B- series) of sulfate anions in the background electrolyte [3].

Among the three Al-containing phases {Al(OH)₃, AlOOH, and Al₂O₃}, the Al(OH)₃ phase played the main role in the adsorbate purification from selenate under all applied experimental conditions except for one. The sample B(I) (SeO₄²⁻+SO₄²⁻ at pH=8.5) was characterized by the unchanged ratio of the two phases {Al(OH)₃/AlOOH} compared to the initial (virgin) sample. This observation correlates with the greater involvement of the Mg(OH)₂ phase compared to the other samples having different pH values. The role of Al(OH)₃ increased as the pH decreased [3].

In the sulfate-free samples (A), the intensity of Al(OH)₃-phase involvement in selenate extraction was greater than in the SO₄²⁻-containing samples (series B) as reflected by stronger decrease of the respective XPS-features, see Fig. 1. Conversely, the contribution of the interlayer carbonate ions was stronger in the sulfate-containing experiments (B-series) compared to the sulfate-free (A) ones as confirmed by the C 1s XPS spectra (see [3]).

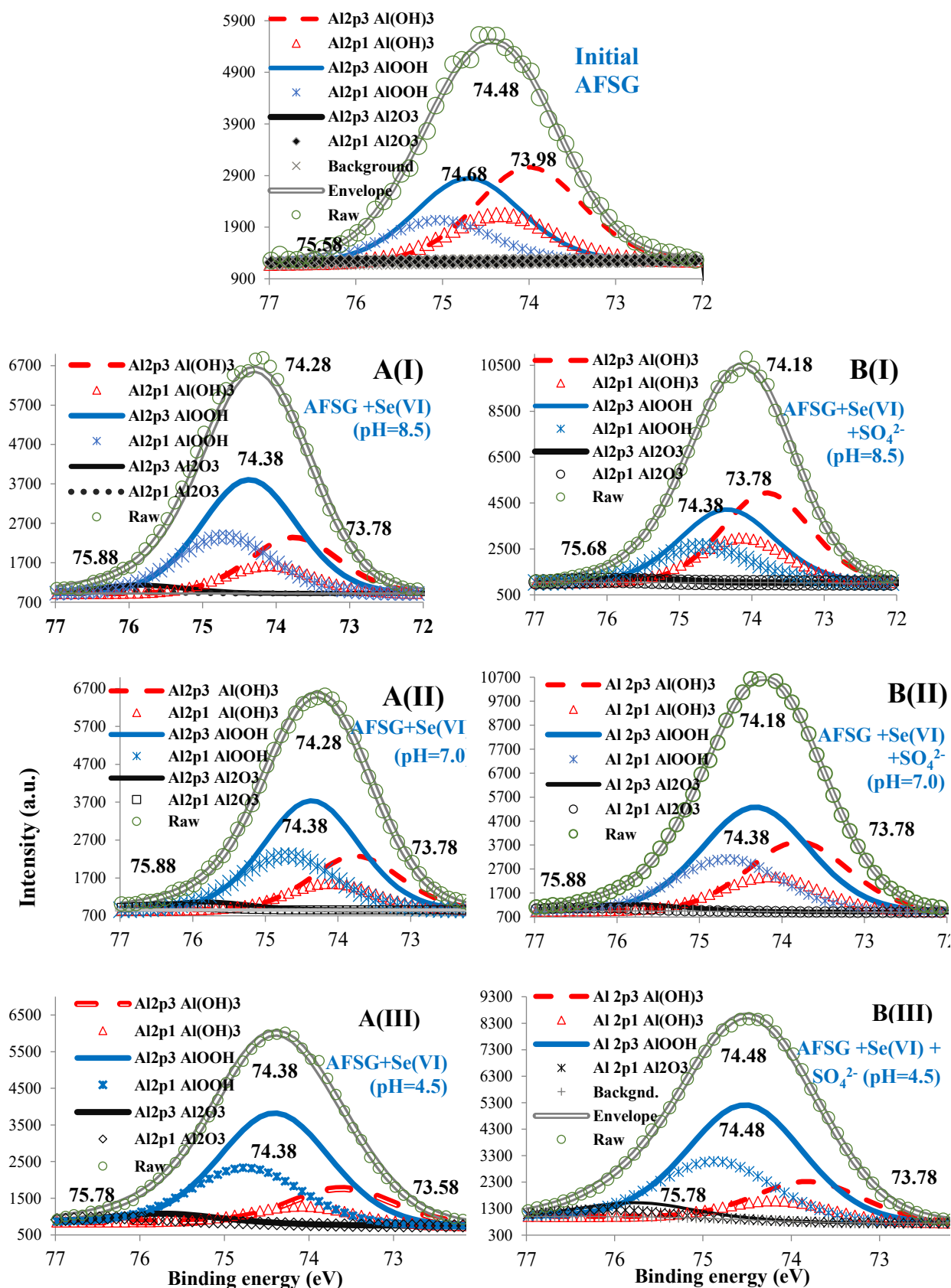


Fig. 1. The Al 2p XPS spectra in the initial Mg-Al-CO₃ LDHs (AFSG) and with SeO₄²⁻ adsorbed in the absence(A)/presence(B) of sulfate at pH= 8.5 (I), 7.0 (II) and 4.5 (III).

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Under both, the sulfate-free (A) and sulfate-containing (B) experimental conditions, the contribution of the interlayer CO₃²⁻ of Mg-Al LDHs was bigger at the lower-pH value batches as demonstrated by the reduction of the carbonate-assigned XPS bands in C 1s XPS spectra [3].

It is noteworthy that regardless of the presence/absence of SO_4^{2-} , at the equal concentrations of H^+ and OH^- in aqueous solutions ($\text{pH}=7.0$), the anion exchange of the interlayer carbonate with aqueous selenate was milder (softer) than at domination of either H^+ or OH^- in the solution. On the other hand, in neutral solutions, the influence of aqueous sulfate on selenate sorption was stronger compared to the alkaline and especially acidic adsorbates [3]. For the first time, it was noted that the presence of SO_4^{2-} in adsorbate shifts the Se 3d binding energy in the Se(VI)-adsorbed layered material regardless of the level of sulfate uptake. However, the shifts of energy were significant in alkaline and acidic suspensions, but very small at $\text{pH}=7$ [3].

This part of the work was the first report showing that localization of Se(VI) and Se(IV) in the interlayer space brings the Se 3d binding energies closer together in the XPS spectra of Se(VI)- and Se(IV)-sorbed Layered double hydroxides. It was also the first observation of the importance (the role) of H^+/OH^- in the removal process of aqueous anions on such layered inorganic anion exchangers, which even changes the molecular mechanism of sorption [3]. Further, this work was a contribution to the XPS database, which previously did not contain any information on the Se 3d binding energies for Se(VI)/Se(IV) anions adsorbed to any layered double hydroxides and localized in its interlayer space [3].

Affinity (and adsorptive removal) of aqueous anions to inorganic ion exchange adsorbents is predefined by the adsorption mechanism. High adsorptive capacity accompanied by high adsorptive affinity is usually a result of a chemisorption mechanism, the formation of real chemical binding of aqueous anions to the material surface via inner-sphere complexation. This well-known distinction was also reflected in the removal performance of Se(IV)-vs-Se(VI) on the investigated Mg-Al LDHs as a function of competing SO_4^{2-} and pH value. The uptake of HSeO_3^- (removed on this material via chemisorption mechanism) was outstanding based on the literature data, while the adsorption of SeO_4^{2-} (attracted via physisorption) was high enough.

Adsorption of selenite (HSeO_3^-). The influence of the (background electrolyte) competing sulfate anions on the removal of both selenium aqueous species was principally different [3,4]. As for the uptake of selenite in the presence of sulfate, it was found that SO_4^{2-} (attracted via physisorption even increased the removal of selenite (HSeO_3^-) (adsorbed via chemisorption) on this Mg-Al- CO_3 LDHs sample, which was stipulated by the difference in their (complementary) sorption mechanisms [4]. The presence of sulfate enhanced the participation of the interlayer carbonate in the uptake of Se(IV), which was deepened at the lower pH values [4].

Although the surface of the Mg-Al- CO_3 LDHs sample is abundant with Mg oxide/hydroxide phases, which undoubtedly initiate the interaction at the interface between the aqueous ions and the solid adsorbent, these Mg phases do not adsorb selenite ions via inner-sphere complexation. The chemisorption binding of HSeO_3^- was performed by the Al-based phases in all experimental batches, A-series (sulfate-free) or B (sulfate-present). In particular, aluminum hydroxide $\{\text{Al}(\text{OH})_3\}$ as the phase retaining Se(IV) anions on the material surface at the final stage {as confirmed by the decrease of Al 2p XPS peaks in the spectra assigned to the aluminum phase of $\text{Al}(\text{OH})_3$ when compared to the spectra of the original sorbent (not used in adsorption experiments). The more significant decrease in the Al 2p XPS peaks assigned to $\text{Al}(\text{OH})_3$ phase in A-series samples compared to series B was explained by greater participation of the interlayer carbonate in the removal of selenite in samples B, which led to a certain decrease in the chemisorption function (at the expense of the anion exchange function) [4].

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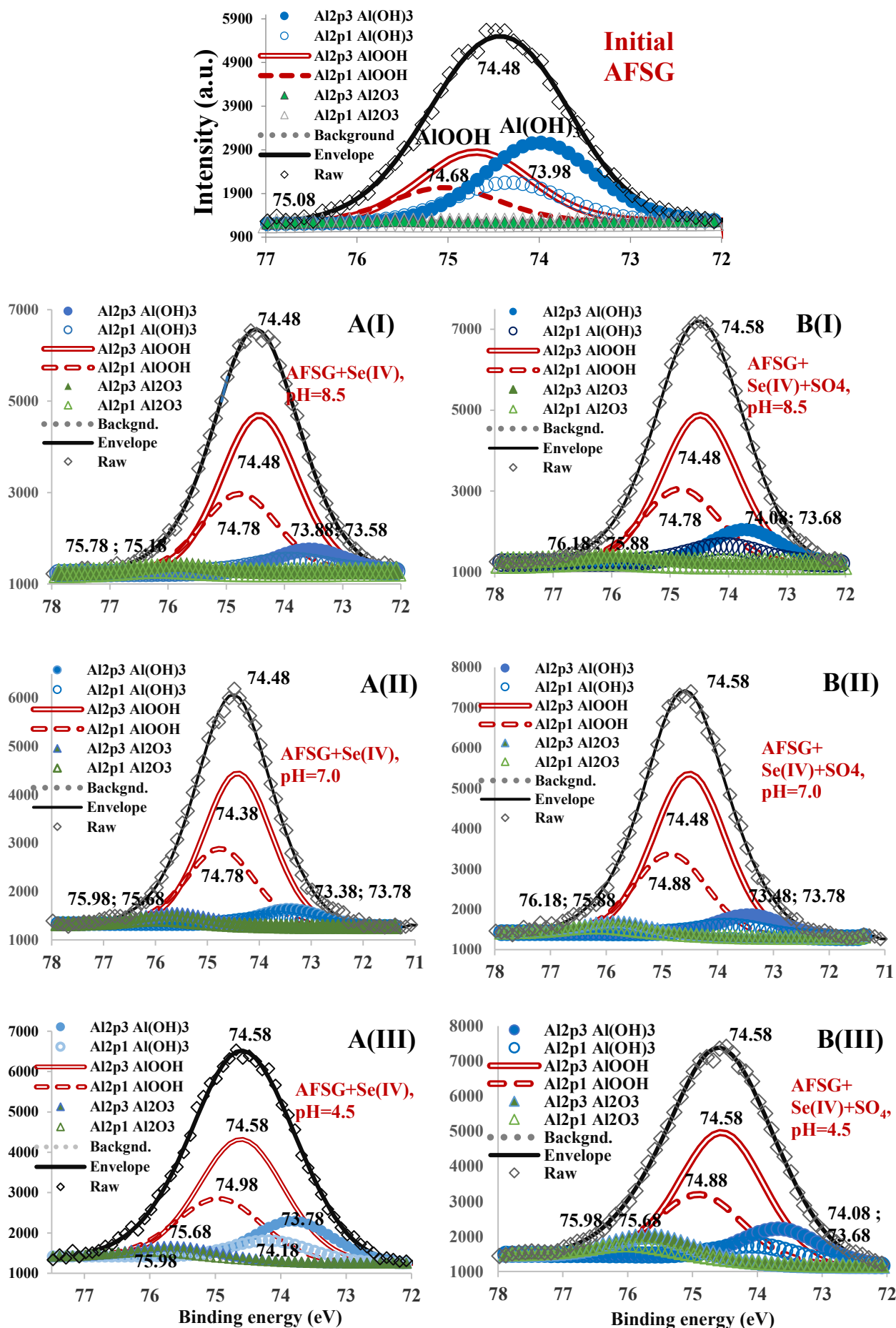


Fig. 2. The Al 2p XPS spectra in the initial Mg-Al-CO₃ LDHs sample (named AFSG) and with sorbed HSeO₃⁻ in the absence(A)/presence(B) of sulfate at the pH=8.5 (I), 7.0 (II) and 4.5 (III).

Conclusions

A comparative analysis of the XPS-based data resulted from the studies of the Se(IV) sorption [4] and the Se(VI) uptake [3] on the same sample of Mg-Al-CO₃ LDHs made it possible to identify how the mechanisms of physical sorption and chemisorption differently change the XPS spectra of the solid material phase, which holds the removed anions at the final stage of the adsorption process. Detailed XPS-based surface analysis allowed us to find out that despite the leading role of Mg-oxide phase (abundant on the surface) at the initial stage of the interfacial reactions, the Al-oxide-based component of Mg-Al LDHs is the phase holding both Se species at the final step. Due to having the previous EXAFS-based study [2], it was noted for the first time that localization of adsorbed anions (selenate and selenite) in the interlayer space of LDHs (here, Mg-Al-CO₃ LDHs) closes the Se 3d binding energies in the respective XPS spectra [3]. As a consequence, a contribution to the XPS database (which did not contain such information yet) has been made [3]. For the first time it has been demonstrated that chemical binding (chemisorption, called also inner-sphere complexation) of anions (HSeO₃[−]) does not affect the position of the envelopmental peaks of the entire sorbing component of the material (such as all Al-phases together), but significantly changes the peaks parameters of a certain sorbing phase {in this study, it is the Al(OH)₃ phase} [3,4]. Conversely, physical sorption of dissolved anions (SeO₄^{2−}) shifts mainly the binding energy of the envelopmental peaks, which covers the entire respective component of the solid phase that removes the dissolved anion (in this work, it is all Al-based oxides/hydroxides which make up the Mg-Al LDHs sample) [3,4]. Based on the results shown in both articles [3,4], a methodological idea (methodological approach) has been proposed for the first time regarding the use of XPS analysis to establish the molecular sorption mechanism by reliably distinguishing the chemisorption pathway from the physical sorption process [4].

Acknowledgments

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Intelligent Flowmeter Based on the Film Method of Gas Flow Measurement for Environmental Monitoring

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Abstract. *The causes of errors in the measurement of small and micro gas flow rates by the film method are analyzed, and measures to minimize them are proposed. An intelligent flow measuring installation with an error of 0.25% in the range of $0...25.0 \cdot 10^{-6} \text{ m}^3/\text{s}$ was developed. The installation for calibration of high-precision flowmeters and gas flow transmitters, gas mixture synthesizers for modern process control systems, including environmental monitoring, is designed.*

Keywords: intelligent flow measuring installation, measuring pipe, film flowmeter.

Introduction

The effectiveness of automated process control systems significantly depends on the amount of primary information about the course of such processes and is determined by the level of development of control and measuring equipment [1-3]. Thus, in the design of automated control systems for modern technological processes that require the measurement of small and micro gas flows [4-9], as well as for the metrological support of gas analytical equipment, in particular, synthesizers of gas mixtures, design of environmental monitoring systems [10-13] and scientific research [14-19], one of the main problems is the lack of high-precision flow meters for micro gas flows ($0...3.0 \cdot 10^{-6} \text{ m}^3/\text{s}$ in pipes with a diameter of 1...5 mm) and small ($3.0 \cdot 10^{-6}...3.0 \cdot 10^{-3} \text{ m}^3/\text{s}$ in pipes with a diameter of 5...10 mm) gas flow rate measurement devices [20, 21].

The need to measure such gas flows usually arises in the latest technologies, in particular, in the production of fiber-optic cables [21], the manufacture of integrated circuits and microelectronic devices [22], as well as in vacuum engineering processes, in medicine, and in metrological work [6, 8, 17]. Therefore, the development of intelligent high-precision flowmeters for the mentioned flow ranges with stable metrological characteristics is an essential task.

I. Film flowmeters for small and micro flow rates of gases

One of the most promising methods of measuring small and micro flow rates of gases is the film method, on the basis of which a number of film flowmeters (FFM) are built [24,25]. The process of measuring small and micro flow rates of gases using FFM is accompanied by the influence of various factors that lead to errors. The occurrence of additional errors, in addition to errors in determining the volume of the calibrated section of the measuring pipe (MP) and measuring the time of passage of the film through this volume, is caused by changes in atmospheric pressure and temperature of the measured gas flow [20, 21]. Elimination (minimization) of such effects makes it possible to significantly reduce the overall measurement error.

The schematic diagram of the FFM, traditionally used to measure such gas flow rates, is shown in Fig. 1a [21]. The FFM contains the measuring pipe 2 fixed on the tripod 1 with the inlet element 3 for supplying the measured gas and the inlet element 4 for supplying a surfactant

solution, a chronometer 5 and the elastic reservoir 6 with a surfactant solution 7 for forming a film. The flow of the measured gas moves the formed film along the inner wetted surface of the MP. Two marks (lower 8 and upper 9) on the MP limit its calibrated area (volume), the time of film passage between which is measured by a chronometer.

The measurement of gas volumetric flow rate using a FFM is to directly determining the time interval for the film to displace a portion of gas from the calibrated volume, and the value of the volumetric flow rate is determined by the formula [21]

$$Q = V \cdot \tau^{-1}, \quad (1)$$

where Q – volumetric flow rate; V – calibrated volume of the MP; τ – measured time of film movement between the marks of the calibrated volume of the MP.

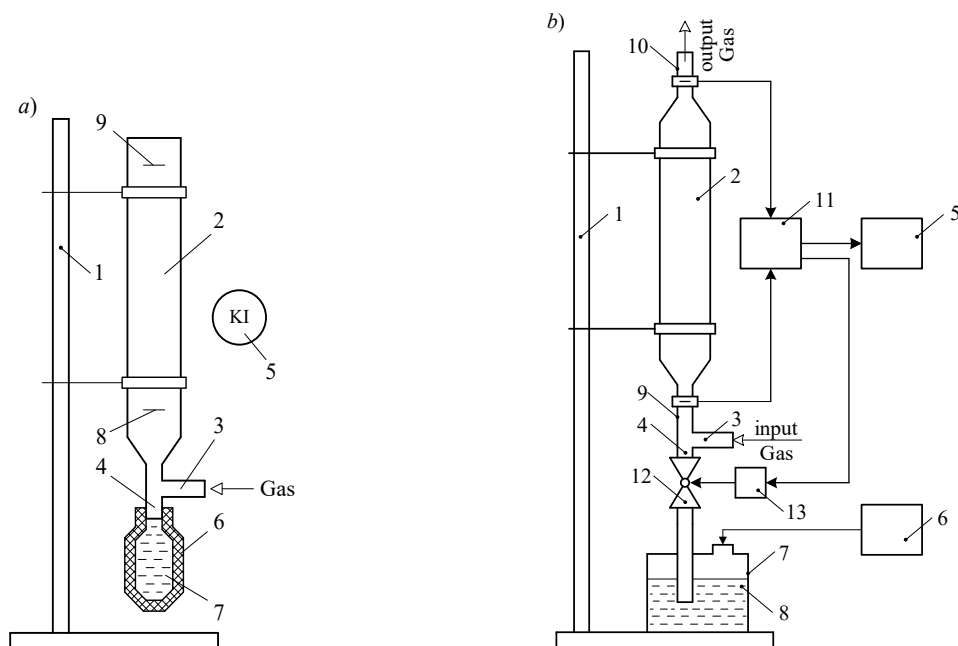


Fig. 1. Schematic diagram of a film flow meter:

1 – tripod; 2 – measuring pipe; 3 and 4 – inlet element for supplying the controlled gas and surfactant solution; 5 – chronometer;

a) basic design: 6 – elastic reservoir; 7 – surfactant solution; 8 and 9 – marks that limit the calibrated volume of the MP;

b) improved automated design: 6 – automated film former; 7 – surfactant solution reservoir; 8 – surfactant solution; 9 and 10 – optoelectric level indicators; 11 – control device; 12 – rotary valve; 13 – electromagnetic drive.

The main error in gas flow measurement using FFM usually does not exceed 1 % [7]. However, due to the inconsistency of the design and application of the FFM with the measurement conditions, additional flow measurement errors occur. For example, as our research has shown, only due to the humidification of the monitored gas with water vapor as a surfactant solvent, the measurement error can reach 3 %.

To form a film in the film flowmeter, aqueous solutions of liquid soap or ammonium oleate are usually used. To prevent foam formation, a silicone emulsion is added to the surfactant solution. The analysis of the operation of such FFM has shown that water evaporates from such a surfactant solution in the MP, as a result of which the volume of controlled gas in the MP increases. This leads to an additional systematic error in gas flow measurement. For example, at atmospheric pressure and a gas temperature of 25 °C, its humidification with water vapor to a relative humidity

of 65 % leads to an increase in volume by 2.15 %, and in the case of gas humidification to full saturation – by 3.3 %. To reduce the impact of this factor, liquids with a higher boiling point than water should be used instead of water as a surfactant solvent. For example, for ethylene glycol with a boiling point of 190 °C, the saturated vapor pressure at room temperature does not exceed 100 Pa, so that even when the gas under test is fully saturated with ethylene glycol vapor, the increase in gas volume at atmospheric pressure and a temperature of 25 °C does not exceed 0.1 % [26, 27].

It should also be noted that some gases react with the surfactant solution. For example, carbon dioxide reacts with an aqueous soap solution, resulting in a decrease in the effective volume of the gas. This also increases the flow measurement error. To eliminate the influence of this factor, it is necessary to use solutions that do not react with the controlled gases. The most versatile solutions are neutral surfactant solutions, for example, solutions of oxyethylated alcohols.

Our research has shown that the following factors mainly affect the measurement error of a film flowmeter:

- accuracy of determining the volume of the calibrated MP section;
- accuracy of measuring the time of passage of the film through this area;
- flow rate measurement conditions (atmospheric pressure and temperature of gas and environment);
- speed of the film movement;
- gas flow through the film;
- physical and chemical properties of both controlled gases and used surfactants and their solvents.

Thus, the aim of the work is to develop measures to improve the accuracy of gas flow measurement by the film method and to create metrological support for high-precision measurement of small and micro flow rates of gases used in automated control systems for innovative technological processes and environmental monitoring.

As a result of the analysis of the above factors and their influence on the components of the flow measurement errors, specific recommendations for the construction of high-precision flow meters and the creation of an intelligent installation for measuring small and micro flow rates of gases have been developed.

It is recommended to use liquids with a boiling point of at least 190 °C, in particular, ethylene glycol, as a solvent of the surfactant in the FFM, and neutral surfactants, such as oxyethylated alcohols, as a film-forming agent.

It is advisable to choose the length of the MP of the film flowmeter within 50...80 cm, provided that the flowmeter is compact in design. To increase the accuracy of determining the volume of the calibrated MP section, it is advisable to make the sections with the limiting marks narrower. To prevent film rupture when moving from a narrower to a wider MP section and vice versa, the ratio of the diameters of its middle expanded and extreme narrowed sections should not exceed 3. To ensure smooth movement of the film along the calibrated section of the measuring pipe and to keep it in a horizontal position, the transitions between the expanded and narrowed sections of the measuring pipe should be made in the form of cut cones with an inclination angle of at least 60°, which are connected to the cylindrical surfaces of the measuring pipe by means of toroidal surfaces.

Taking into account the proposed recommendations and research a high-precision automated film flowmeter was developed. During the development of the installation, all the technical

requirements and application features of the system were taken into account. The schematic diagram of which is shown in Fig. 1b.

The calibrated section of the MP of the developed FFM is limited by optoelectric level indicators 9 and 10 connected through the control device 11 to the chronometer 5, which minimizes the error in measuring the time of passage of the graduated volume by the film between the limiting marks. In addition, in this FFM, the inlet element 4 for supplying the surfactant solution to the MP before the inlet element 3 for supplying gas to it is equipped with a rotary valve 12 with an electromagnetic drive 13 connected to the control device 11, which ensures a hermetic separation of the container 7 with the surfactant solution from the controlled gas flow during the measurement of its flow. This design reduces the component of the measurement error arising from the evaporation of the surfactant solvent.

In addition, the peculiarity of the developed FFM is that the volume of the calibrated section of the MP is determined taking into account the adhesion of the surfactant solution on its inner surface, which minimizes the systematic component of the flow measurement error created by this factor.

To minimize the effect of the error of the film flowmeter of gas transfusion through the film when measuring the flow rate of air or gases with a density greater than the density of air, such gases must be supplied to the MP from below. In this case, the film moves from the lower optoelectric indicator of level 9 to the upper level 10. Conversely, when measuring the flow rate of gases with a density lower than the density of air, it is necessary to supply gas to the measuring pipe from above and the film then moves from the upper optoelectric indicator of level 10 to the lower level 9.

All of the factors discussed above determine the systematic component of the film flowmeter measurement error. This component of the film flowmeter error is mainly influenced by changes in atmospheric pressure, temperature of the controlled gas, and the volume of the calibrated measuring pipe section.

The random component of the FFM measurement error is mainly determined by the instability of the measured flow. Our studies have shown that the random component of the error due to the instability of the measured flow can reach several percent. Therefore, in order to reduce the measurement error of the film flowmeter and its random component, it is necessary to stabilize the measured gas flow.

II. Intelligent flowmeter for small and micro flow rates of gases based on the film measurement method

On the basis of the automated film flowmeter described above and taking into account the requirements for gas flow stabilization, an intelligent installation for measuring small and micro flow rates of gases was developed, the block diagram of which is shown in Fig. 2. The installation includes an automated flow meter placed in a closed enclosure with a temperature stabilization system, as well as a microprocessor device for monitoring and controlling the operation of the installation with displaying the flow measurement results [28]. The setup also contains a gas temperature sensor, a barometer, a gas flow stabilizer, and a section for installing the flow meter under test. The installation is intelligent, since the obtained flow measurement result takes into account, in addition to the main quantities – the volume of the calibrated measuring pipe section and the time of passage of the film through this section, and gas temperature and atmospheric pressure, i.e. parameters of the controlled gas state.

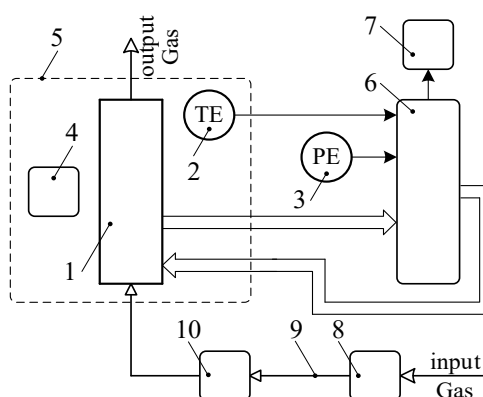


Fig. 2. Block diagram of an intelligent unit for measuring of small and micro flow rates of gases:

- 1 – automated FFM; 2 – gas temperature sensor; 3 – barometer; 4 – temperature stabilization system in the installation housing; 5 – installation housing; 6 – microprocessor control and management device; 7 – device for displaying flow measurement results; 8 – gas flow stabilizer; 9 – site for installation of the flowmeter under study; 10 – the flow meter under test.

Thus, the result of measuring the volumetric flow rate of gas reduced to normal conditions is determined using the microprocessor device of the intelligent flowmeter according to the following formula:

$$Q = \frac{V}{\tau} \cdot \frac{P_b \cdot T_n}{T_c \cdot P_n}, \quad (2)$$

where Q – the volume gas flow rate reduced to normal measurement conditions; V – the volume of the calibrated measuring pipe section; τ – the time of movement of the film along the calibrated measuring pipe section by the controlled gas; P_b – the atmospheric pressure; T_c – the temperature of the controlled gas; $T_n = 293.15^\circ\text{C}$ – the normal temperature; $P_n = 101325\text{ Pa}$ – the normal pressure.

The developed intelligent installation provides measurement of small and micro flow rates of gases in the range of $0 \dots 25.0 \cdot 10^{-6} \text{ m}^3/\text{s}$ with an error of 0.25 %. The installation is designed for calibration and verification of high-precision measuring instruments for small and micro flow rates of gases.

III. Conclusions

Thus, as a result of the technical implementation of measures to eliminate (reduce) the impact of the identified causes of systematic and random components of the measurement error of small and micro gas flow rates, a high-precision intelligent installation based on the film measurement method was developed. The developed installation, due to the determination of the parameters of the state of the controlled gas and the environment (external temperature and atmospheric pressure), as well as due to the stabilization of the gas flow in the process of measuring its flow rate, minimized the components of the flow measurement error, and thus increased the accuracy of measurements. The installation provides measurement of small and micro flow rates of gases in the range from $0 \dots 25.0 \cdot 10^{-6} \text{ m}^3/\text{s}$ with an error not exceeding 0.25 %.

Further promising areas of research in film flowmeter include, in particular, expanding the range of industrial gas flow measurement, improving systems for measuring the time of film

passage through the calibrated volume of measuring pipe, as well as thermostating and calibration. Such research will help to improve both the metrological and operational characteristics of the film flowmeter, which will further enable us to meet the growing demands for measuring small and micro flow rates of gases in the latest technological processes and environmental monitoring systems. This will also help to reduce the cost of their maintenance and operation, which is important for modern industry.

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Granulated slow-release fertilizers based on urea and flue gas desulfurization gypsum

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Abstract. *This paper presents the results of research on a process for the production of a calcium sulphate and urea adduct and a method to slow down the release of nitrogen by coating the fertilizer granules with polymers.*

Keywords: urea, FGD gypsum, granulation, slow release fertilizers.

Introduction

In the years 2010-2012, at the Łukasiewicz Institute of New Chemical Syntheses, as part of a development project, the technology of granulated nitrogen-calcium-sulfur fertilizer based on phosphogypsum and urea containing an adduct of calcium sulphate and urea ($\text{CaSO}_4 \cdot 4\text{CO}(\text{NH}_2)$) was developed [1]. Agricultural plot research at the Institute of Soil Science and Plant Cultivation State Research Institute showed that fertilizers produced according to the developed technology, which were used before sowing, have been characterized by a slight slowdown in the nitrogen release. The pre-sowing used in one dose in rapeseed and wheat cultivation showed no worse yielding effects than ammonium nitrate used in two doses. However, the granules of this fertilizer were characterized by an unfavourable shape, significant porosity, and a rough surface (Fig. 1). The encouraging results of agricultural research prompted us to work on developing the adduct granulation technique and improving the slowing down of nitrogen release [2-5].



Fig.1. Photograph of the adduct obtained in the semi-technical plant test in 2011.

Methodology and test results

The aim of the work was to increase the quality of the adduct granules and to develop an economical method of producing fertilizer with a slow release of nitrogen by coating the fertilizer granules with polymers.

Semi-technical tests of NCaS fertilizer production and granulation were carried out in the pilot unit of Łukasiewicz-INS (Fig. 2).

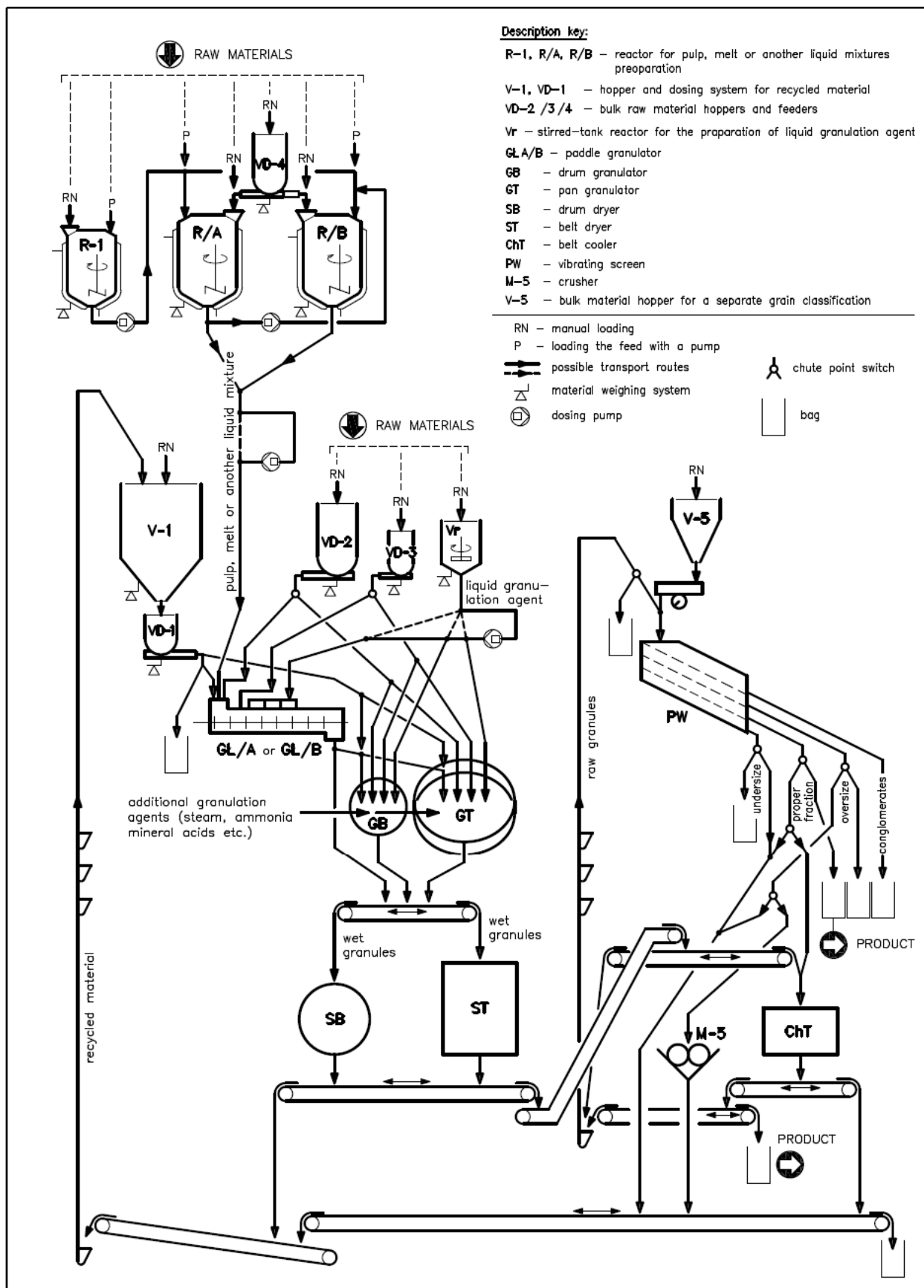


Fig.2. Diagram of a semi-pilot plant for the production of granulated fertilizers at Research Centre at Łukasiewicz-INS.

The basic raw materials used were urea fertilizer (produced by G.A. Z.A. Puławy SA) and synthetic calcium sulphate hemihydrate from the flue gas desulfurization process with a grain size of less than 100 μm , (produced by Dolina Nidy Sp. z o.o.). A urea solution with a concentration of 80-90% by mass was sprayed onto the material in a granulation plate to which recycle and gypsum were continuously dosed at a temperature of approximately 55-65°C. Granules were produced in the granulation pan, fed into a drum dryer and, after classification on sieves, a granulated product (adduct) was obtained. Thanks to the use of the synthetic semi-aqueous gypsum (FGDG) and ground adduct recycling, the adduct granules were obtained with a spherical shape and a fairly smooth surface, which turned out to be useful for applying polymer coatings (Fig. 3).



Fig. 3. NCaS fertilizer granules obtained during semi-technical tests.

The adduct granules were coated with a coating agent using a laboratory coating unit (Fig. 4). The coating agent was applied to the granules in a rotating bed of material (Fig. 4) in 3 layers at a temperature of 80-90°C, maintained by irradiation with an infrared radiator. According to the new EU fertilizer Regulation 2019/1009, the fertilizer polymer coating should decompose by 90% in soil conditions within 4 years [6].



Fig. 4. Laboratory unit for coating fertilizers with a Teflon covered drum and an infrared radiator (150W).

The release rate of urea nitrogen from samples of fertilizer granulates was determined in the static tests by measuring the concentration of urea, by measuring the refractive index, in the solution that was in contact with the fertilizer sample at specific time intervals under conditions according to the methodology used in Japanese laboratories [7], (10 g of fertilizer / 200 g of water, differing slightly from those described in the EN 13266:2003 standard [8] where 10 g of fertilizer / 500 ml of water is used).

The NCaS granules were coated three times with coating agent (Fig.5) in a total amount of 4% by mass. The time of applying and hardening of the 3 layers of the coating did not exceed 50 minutes. The release time of 75% of nitrogen from this sample in the static test was approximately 90 days (Fig. 6).



Fig. 5. Photo - view of coated NCaS fertilizer granules.

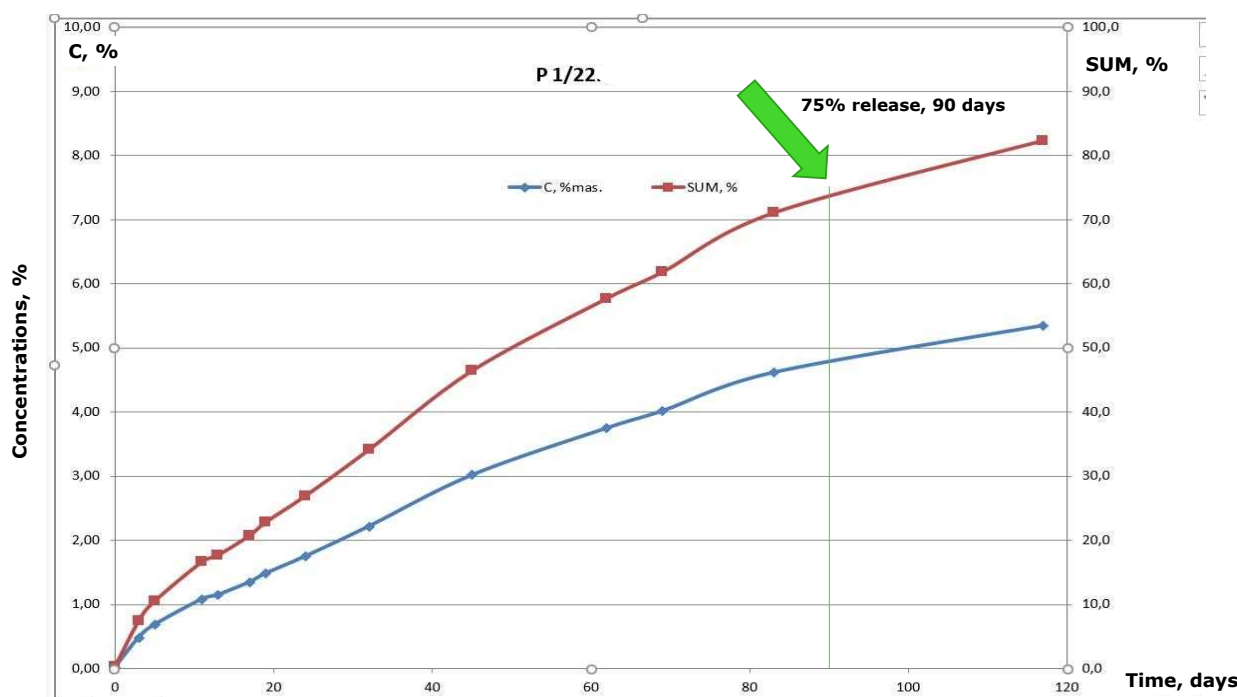


Fig. 6. Concentration (C, %) and urea release rate (SUM) from sample no. 1/22. (nitrogen release tests started immediately after the coating was made).

The degree of urea release SUM (in %) was determined as the ratio of the percentage concentration of urea of the tested sample solution (C) to the concentration of the solution obtained against the parallel ground reference sample (Cz).

$$SUM = \frac{C}{Cz} \times 100\% \quad (1)$$

Conclusions

1. An economical method of production of granulated nitrogen-calcium-sulfur (NCaS) fertilizer with slow nitrogen release, containing 27% N, 11% Ca, 8.5% S, was developed.
2. The NCaS fertilizer contains 4% (by weight) of epoxy resin. The production process is feasible. Further works – scaling up of the coating process.
3. The production process is feasible. Further works will focus on scaling up the coating process.
4. The nitrogen release time is over 3 months, it can be adjusted according to the quantity/thickness of the coating.
5. Agricultural pot tests on the rapeseed showed excellent effectiveness of the developed fertilizer, more than doubling the yield of rapeseed seeds compared to control objects.

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TO THE MEMORY OF THE OUTSTANDING SCIENTIST AND PEDAGOGUE OF LVIV POLYTECHNIC ZORIAN HRYHOROVYCH PIKH	477

SPONSORS AND PARTNERS



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KARPATNAFTOCHIM Ltd. was founded in October 2004. Legal address ID code: 33129683.

The only participant of the Company is KARPATY CHEMICAL B.V., legal entity under the laws of the Kingdom of the Netherlands, whose seat is: Helsinkilaan, 4, 3446 AH Woerden, the Netherlands.

KARPATNAFTOCHIM Ltd. is highly developed economic complex for the production of petrochemical and chemical products. The only producer in Ukraine of ethylene, propylene, benzene, C9-cut, polyethylene, as well as caustic soda and suspension polyvinylchloride. The latter are the new products of the company.

The multi-branched network of automobile roads and railways, close distance to borders with Poland, Romania, Hungary, Slovakia, availability of ethylene pipe line between KARPATNAFTOCHIM Ltd. and Tiszai chemical works in Hungary creates favourable preconditions for the integration of the enterprise to the European industrial and trade activity.

High quality of products is provided by highly qualified staff of petrochemists as per international integrated management standards ISO 9001, ISO 14001, OHSAS 18001.



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Limited liability company “Polikom.” is innovative, client-oriented production company which develops dynamically. It was founded in 1997 due to the initiative of a group of experts who had more than 30-year scientific and production experience in the sphere of polymer synthesis and processing. Nowadays Polikom is the leader in CIS in development of PVC-based compositions; production of the wide range of commodity PVC-plastisols and PVC-granulates for wallpaper industry, linoleum, artificial leather, sealing gaskets for food and technical designation; as well as production of roll technical materials (awnings, banners, geomembranes), protector working gloves, souvenir products etc. Polikom operates its great experience, which is strengthened by its own researches and following of new tendencies, and constantly improves its products and expands its stock.

As for today our company produces also organic pigment pastes for colouring of PVC-plastisols, water-based systems for wallpaper production, pigment pastes for their colouring, undusted effect-pigments and other multifunctional additives for different usage spheres according to their individual properties.



Inter Syntez LLC

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Inter Syntez is a leading supplier of food additives for meat, confectionery, bakery, dairy and other food industries. The company is a developer and manufacturer of «GELEX» stabilizing system.

Our company offers tara gum and locust bean gum as an effective substitution for guar gum.

Inter Syntez is well known for its research in disinfectants production sphere. Trademarks «Crystal 700», «Crystal 900» and «Crystal 1000» successfully compete with imported analogues in Ukraine and abroad.

One of our company's main activities is selling various brands of hydrogen peroxide. We use our own methods for stabilizing hydrogen peroxide, particularly for industries using «TetraPak» and «KombBlok».



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**TO THE MEMORY OF THE
OUTSTANDING SCIENTIST AND
PEDAGOGUE OF LVIV POLYTECHNIC
ZORIAN HRYHOROVYCH PIKH**



Professor Zorian Hryhorovych PIKH was born on June 25, 1950, in the city of Horodok, Lviv region. From 1967, he studied at the Faculty of Organic Chemistry Technology at Lviv Polytechnic, after graduating with honors in 1972, he remained at the Department of Technology of General Organic and Petrochemical Synthesis, where he progressed from junior research fellow to the department head. From 1978, Zorian PIKH was a senior research fellow, from 1979 - assistant, from 1986 - associate professor, and from 1994 - professor of the department.

In 1978, he defended his candidate dissertation in the specialty of organic chemistry on the topic "Oxidation of higher alkylacrolein with oxygen and peroxides," and in 1994 - his doctoral dissertation in the specialty of technology of organic synthesis products on the topic "Selective oxidation of unsaturated compounds with bound oxygen." In 1995, he was awarded the academic title of professor of the Department of Technology of General Organic and Petrochemical Synthesis.

Since the department provided studying in two specialties - chemical technology of organic substances and technology of fermentation production and winemaking, in 1996, by order of the rector of Lviv Polytechnic, the department was renamed to the Department of Technology of Organic Products. In 2001, Professor Zorian PIKH became head of the department. During 2007-2014, he also served as vice-rector for R&D work at Lviv Polytechnic.

Professor Zorian PIKH was a renowned specialist in the field of kinetics, mechanisms of oxidation reactions of organic compounds, mathematical description and methodology of research of complex chemical reactions and processes. Based on the results of systematic research, he formulated and substantiated the concept of the interrelation of mechanisms of oxidation of organic compounds by various oxidants. In 2015, by decree of the President of Ukraine, he was awarded the honorary title of Honored Science and Technology Figure of Ukraine.

Under the supervision of Zorian PIKH, 3 doctoral and 8 candidate dissertations were defended.

He died on November 18, 2021, and was buried in Lviv at Yaniv Cemetery.

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