2nd INTERNATIONAL SCIENTIFIC CONFERENCE

CHEMICAL TECHNOLOGY AND ENGINEERING

PROCEEDINGS

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2nd International Scientific Conference
«Chemical Technology and Engineering»

PROCEEDINGS

Ukraine, Lviv, June 24-28th, 2019

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The Conference Organizers:

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

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

Department of Chemical and Process Engineering, Faculty of Chemistry, Rzeszow University of Technology (Rzeszow, Poland);

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

Division of Bioprocess and Biomedical Engineering, Faculty of Chemistry, Wroclaw Universiy of Science and Technology (Wroclaw, Poland)

with the participation of

Scientific Society of Students, Doctoral Candidates and Young Researchers of Institute of Chemistry and Chemical Technologies of Lviv National Polytechnic University;

Alumni Association of Lviv Polytechnic National University;

Ukrainian Association of Chemical and Food Engineering (CFE-UA).

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Greetings of the Program Committee's Chairman of the 2nd International Scientific Conference «Chemical Technology and Engineering», **Rector of Lviv Polytechnic National University, DSc, Professor Yuriy Bobalo**

Dear participants!

Two years have passed – and we are glad to greet you again in the walls of the oldest technical higher educational institution of Eastern Europe – Lviv Polytechnic National University!

Chemistry is one of the scientific direction that originates from the creation of our University. I am sure that a big scientific event in Lviv Polytechnic, dedicated to the problems of chemical technology and engineering, will contribute to further development of the field, actual tasks solving, experience exchanging and establishing of cooperation between chemists of Ukraine and the whole world.

I wish you fruitful work, exciting discussions and scientific achievements!

Greetings of the Organizing Committee's Chairman of the 2nd International Scientific Conference «Chemical Technology and Engineering», **Head of the Department of Chemical Engineering, Lviv Polytechnic National University, DSc, Professor**

Volodymyr Atamanyuk

Dear colleagues!

Thank you for your interest and participation in our biannual conference!

This year we have a great pleasure in celebrating the jubilee of the Department of Chemical Engineering of Lviv Polytechnic National University within the conference. Already for 70 years our Department has been teaching specialists in the field of chemical technology and engineering, and became a cradle and a second home for many scientists.

We sincerely congratulate all the participants of the conference and believe that our scientific event will become a traditional place for you to exchange thoughts, experiences, search for new colleagues and just friends!

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PLENARY PRESENTATIONS

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Dean of Faculty of Chemistry, Head of the Department of Chemical and Process Engineering, Rzeszow University of Technology, Poland

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Professor **Artur Badyda**

Head of the Department of Informatics and Environment Quality Research, Warsaw University of Technology, Poland

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Professor **Anna Chrobok**

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SCORPIONATES WITH REAL STING

Doctor **Roman Kresinski**

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Academician **Yuriy Sniezhkin**

Member of National Academy of Sciences of Ukraine, Director of Institute of Engineering Thermophysics of National Academy of Sciences of Ukraine, Ukraine

PARTICLES AND LUNGS – WHERE CHEMICAL ENGINEERING MEETS MEDICINE

Professor **Tomasz Sosnowski**

DSc, Vice-Dean for Scientific Research of the Faculty of Chemical and Process Engineering, Warsaw University of Technology, Poland

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Associate Professor **Wladimir Suprun**

Head of Laboratory of Heterogeneous
Catalysis, Senior Research Scientist,
Institute of Chemical Technology, Leipzig
University, Germany

PROCESS STAGES ENERGY EFFICIENCY INCREASING IN HIGH CAPACITY AMMONIA PRODUCTION PLANTS (1360 – 1420 T NH_3/DAY)

Professor **Leonid Tovazhnyanskyy**

Honorary Rector of NTU “KhPI”,
Corresponding Member of the National
Academy of Sciences of Ukraine, Head of
the Department of Integrated Technologies,
Processes and Instruments, Ukraine

YOUNG CHEMIST’S SCHOOL PRESENTATIONS

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Associate Professor **Oleksandr Ivashchuk**

Associate Dean for Master's Studies for Organizational and Educational Work of the Institute of Chemistry and Chemical Technologies, Lviv Polytechnic National University, Ukraine

C4 CHEMISTRY: USING OF RENEWABLE RAW MATERIALS FOR THE PRODUCTION OF ENERGY AND CHEMICAL PRODUCTS

Associate Professor **Wladimir Suprun**

Head of Laboratory of Heterogeneous Catalysis, Senior Research Scientist, Institute of Chemical Technology, Leipzig University, Germany

START-UP DEVELOPMENT

Wojciech Wodo

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CONTINUOUS IMPROVEMENT IN EDUCATION OF CHEMICAL ENGINEERS AND RESEARCHERS IN THE UNITED STATES

Taras Yurkiv

Retired Senior Process Engineer,
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Department of Chemical Engineering of Lviv Polytechnic National University originates from 1949. Researches of the Department of Chemical Engineering has 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 the specialists in «Equipment of chemical industries and enterprises of building materials», «Processes and equipment of chemical plants» and «Computerical chemical engineering».

In recent years the Department has been actively developing a new line of work that is associated with numerical modeling of the 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 analyze of the equipment of chemical, food, pharmaceutical industries and the industry of the building materials production.

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 the industrial processes
- optimization of hydrodynamics and heat transfer in industrial installations – designing of the technology systems (software simulation: SOLIDWORKS, ANSYS FLUENT)
- CFD-modeling

ŁUKASIEWICZ Research Network – New Chemical Syntheses Institute

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ŁUKASIEWICZ Research Network – New Chemical Syntheses Institute (INS) seated in Pulawy, Poland is a state research institute with a long lasting tradition.

ŁUKASIEWICZ Research Network – New Chemical Syntheses Institute is one of the best Polish research institutes. It enjoys a good reputation and INS trade mark is well known in Poland and abroad.

The principal aim of the Institute is work for chemical industry, mainly its fertilizer and inorganic branches, which leads to making innovations and higher competitiveness of companies operating in chemistry and chemical technology areas. INS carries out research and development work in close partnership with industry employing high qualified staff and maintaining latest standards applying to research methods and procedures. It has the unique advantage of carrying research works in pilot plants and directly on industrial plants. The Institute co-operates with all fertilizer producers in Poland and many abroad. This fruitful cooperation resulted in numerous licences sold i.a. to Russia, Germany, Bulgaria, Czech Republic, Croatia, Ukraine, Belarus, and Hungary. Our catalysts are purchased worldwide by 18 countries, including Columbia, Chile, and USA.

Scope of activities

Research and development work in the field of chemical and biological sciences with a special interest in chemical engineering including:

- **synthesis and inorganic technology** (synthesis gases, hydrogen, ammonia, nitric acid and nitrogen compounds, phosphoric acid and phosphorous compounds, silicon compounds, mineral fertilizers, mineral feed additives)

- **synthesis and organic technology** (urea and methanol derivatives, biodegradable polymers based on plant raw materials, polyurethane foams on melamine basis)
- **biotechnology** (extraction of plant products with CO_2 under supercritical conditions)
- **applied catalysis - heterogeneous catalysts, sorbents, catalyst supports**
- **environmental protection**
- unit operations: granulation, absorption, adsorption, crystallization, filtration.

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
- high pressure research apparatus
- chemicals for fertilizer conditioning, impregnation (fire retardants), steel degreasing and steel phosphating.

RZESZOW UNIVERSITY
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PhD. DSc. Wojciech Piątkowski, prof of RUT
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PhD. Renata Muca
PhD. Izabela Poplewska
PhD. Grzegorz Poplewski
MSc. Karolina Leś
MSc. Grzegorz Król

Research conducted at Department

- Separation processes (chromatography, adsorption, crystallization) of micro- and macromolecules
- Optimization and integration of technological processes
- Design of technological systems (simulation programs: ASPEN PLUS, HYSYS, HX-NET, FLUENT)
- Research and modeling of reactor processes in homo- and heterophasic systems, (heterogeneous catalysis)
- Experimental research and computer modeling of operations involving loose materials.

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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 in 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.

Wroclaw University of Science and Technology

Division of Bioprocess and Biomedical Engineering

www.pwr.edu.pl

www.prochembio.pwr.wroc.pl

Wroclaw University of Science and Technology (WUST) is the leading scientific and educational centre in Poland. Development of the University is confirmed by research potential, didactics at the highest level, innovation and also cooperation with industry. The University educates specialists who are valued and sought after in the labour market.

Wroclaw University of Science and Technology is an inheritor of the tangible property of the German University Königliche Technische Hochschule Breslau, and also the intellectual and scientific heritage of Lviv Polytechnic. The University, as Wroclaw University of Technology, has been operating since 1945.

Today it is one of the biggest and best technical universities in the country with 34,000 students being educated by 2000 academic teachers in 16 faculties: Architecture; Civil Engineering; Chemistry; Electronics; Electrical Engineering; Geoengineering, Mining and Geology; Environmental Engineering; Computer Science and Management; Mechanical and Power Engineering; Mechanical Engineering; Fundamental Problems of Technology; Microsystem Electronics and Photonics; Pure and Applied Mathematics; Technology and Computer Science; Technology and Engineering; Technology and Natural Sciences.

Division of Bioprocess and Biomedical Engineering (Z-11) led by Prof. Anna Trusek-Hołownia, Ph.D, D.Sc. is one of a several research group at Department of Chemistry (W3).

For years studies conducted by researchers of Z-11/W3 combine the knowledge of chemical engineering and industrial (white) biotechnology. The main subject of research are bioreactor processes (both microbiological and enzymatic) conducted in reactors 0.5-25 liters in volume. These bioreactors are often integrated with membrane processes. Enzymatic reactions are carried out with the use of native catalysts or preparations with a catalyst immobilized by sorption, covalent bonding or cross-linked in hydrogel. Typical membrane processes are also carried out in Z-11 with a focus on separation of reaction mixtures, natural media from food industry or waste streams (industrial wastewater).

Since 2011 scientific activity of the Division has been extended to the modeling of transport of active substances (e.g. drugs, hormones, etc.) and mass transport with reaction. This will allow us to apply principles known in chemical engineering to pharmacokinetics at the drug carrier-body fluid level.

The aim of studies is to carry out the (bio)technological and biomedical process, and then with the help of tools used in chemical engineering to prepare a mathematical description of the model characteristics in order to find the optimal range of parameters affecting the considered process.

COMPUTER SIMULATION IN THE CHEMICAL TECHNOLOGY AND ENGINEERING

Particles and lungs - where chemical engineering meets medicine

Sosnowski Tomasz R.

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Abstract* – *Paper draws attention to chemical engineering applications in the problems of drug delivery by inhalation, i.e. in atomization of liquids, preparation of functional powders and their aerosolization, aerodynamic design of inhaling devices, and finally – flow and mass transfer processes in the layers of lung fluids (bronchial mucus and pulmonary surfactant).

Keywords – aerosol, generation, inhalation, CFD, surface effects, lung fluids.

Introduction

The XXI-th century paradigms of chemical engineering emphasize the importance of intensification of the momentum, heat, and mass transfer processes by employing novel approaches which may be based, e.g. on mimicking the phenomena found in the living world ("bio-inspiration"). For instance, microfluidic systems which have been demonstrated to be very effective in conducting mass transfer processes with a high selectivity [1] are inspired by living microsystems which are characterized by extremely high surface-to-area ratio and laminar flow-controlled mass exchange (e.g. oxygen transport from blood capillaries to the tissues, gas-exchange across air/blood barrier in the pulmonary alveoli). This is why the bioengineering becomes very important in the modern chemical and process engineering/technology. Such definition of "bioengineering" has much broader meaning than "biotechnology" or "bioprocess engineering", and it often relates also to the application of the engineering-based analysis of fluid flow and mass transfer phenomena in the close relation to medicine.

The current paper is focused on the highlighting of the problem of particle inhalation and their interactions with the respiratory system, and analyzing these processes by using the phenomenological approach and scientific tools of chemical engineering.

Characteristics of inhaled aerosols and definition of engineering challenges

Inhaled particles constitute a dispersed colloidal system of polydisperse micro- or nanometer-size objects suspended in the air ("aero" + "sol"). While inhaled, they travel with the air through the complex system of air ducts of the bronchial tree where they can be gradually removed (captured) due to the action of several deposition mechanism, which are essentially identical to those met in the industrial gas cleaning devices (dust separators). Regional deposition in the respiratory tract depends on many factors, including particle size, shape and density, but also the local and temporal air velocity, and the local geometry of the air ducts of the breathing organ (bending, division, narrowing, etc), Figure 1.

When inhaled particles are potentially toxic - such as aerosols generated by combustion or other industrial processes - their local deposition in different parts of the respiratory tract is responsible for many health effects, including airway inflammation, asthma, COPD, fibrosis, and lung cancer. It is commonly agreed that only particles smaller than 10 μμm are inhalable, i.e. can pass the mouth/throat region ("oropharynx"). Penetration to the deeper regions of the bronchial tree ("lung periphery") requires particles or droplets smaller than 5 μm which are often called "fine particles". In the environmental toxicology it has been established that, so called PM2.5 (particulate matter with size below 2.5 μm) form the most harmful aerosol fraction.

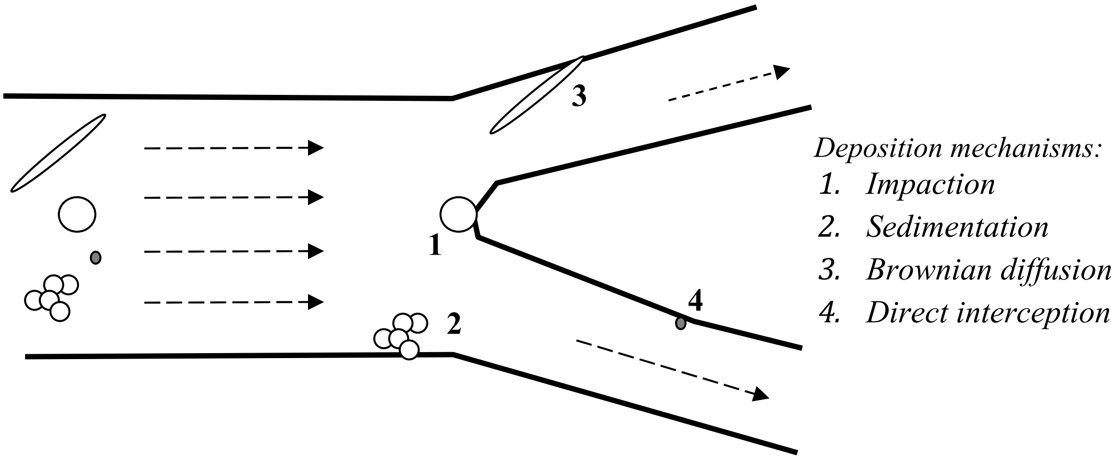

Fig. 1. Schematic deposition of aerosol particles with different shapes and sizes in a bronchial bifurcation.

On the other hand, aerosol particles or droplets may be used also as carriers of medicines (drugs) administered to the respiratory system. They can be used to treat pulmonary diseases locally or to deliver drugs to the whole body via the air/blood barrier [2, 3]. For these therapeutic aerosols we need to predict the spatial distribution of deposition to correctly design the most beneficial drug delivery system (Figure 2).

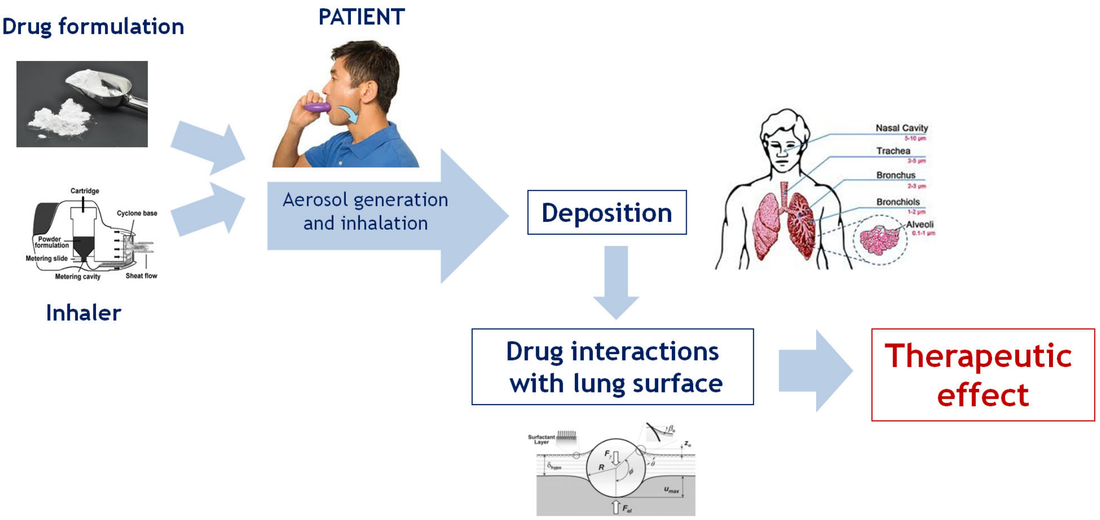

Fig. 2. A scheme of inhalation as a route of drug delivery.

As seen in Fig. 2, the essential engineering challenge of drug delivery by inhalation is designing the proper aerosol generating system composed of the carrier (drug formulation) and the aerosolization device (inhaler) capable of producing the inhalable aerosol dose with a desired particle size just before the moment of drug administration.

Aerosol drug carriers and the dispersing devices (inhalers)

Inhaled drugs may be carried inside aerosol composed of liquid droplets or solid particles. Consequently, such aerosols are produced in inhalers either by the process of liquid atomization (spraying, known as "nebulization of drugs") or dispersion of powders. Each type of inhaler requires careful design to assure reproducibility of the quality (i.e. particle size distribution) and the quantity (i.e. dose) of emitted drug, ease of use, durability and a reasonable price.

Nebulizers which spray liquid medicines (originally being a solution or suspension), utilize compressed air, ultrasonics or vibrating mesh technology to produce mist of droplets within the micrometric size range. The quality of aerosol mist often depends on the physicochemical properties of nebulized drugs, mainly, the viscosity, surface tension and ionic strength [4-6]. The main advantage of nebulizers is that they are used during normal (tidal) breathing, without special inhalation maneuvers, which make them suitable also for toddlers or people with disabilities. Recently some novel aspects of using these devices have been identified and discussed [7].

Dry powder inhalers (DPIs) are a broad class of medical devices used to disperse powders. They are portable but usually require special inhalation maneuver to assure good generation of aerosol and efficient drug delivery to the lungs. The main problem with DPIs is that they operate properly only if a certain inspiration effort is achieved for producing the inhalable dose, however sometimes such effort cannot be obtained by users (patients). As a consequence the drug may be not delivered as prescribed (aerosol emission is too small, particles are aggregated and too big in size). Various DPIs have different internal aerodynamic resistance which make them even more difficult to use reproducibly by different patients [8]. It is therefore essential to look for the methods to improve the performance of DPIs. One strategy is to optimize the properties of powder to make it easier to disperse. “Particle engineering” is the most suitable approach to do so, and it can use, e.g., the optimized spray drying process to obtain powders with controlled properties regarding their morphology, stability and aerosolization properties [9-12]. The spray drying technique also allows to produce particles with the ordered structure [13] and with certain functionality after deposition on the lung surface [14-16]. An example of a structurized microparticle obtained in our laboratory via controlled spray drying is shown in Fig. 3.

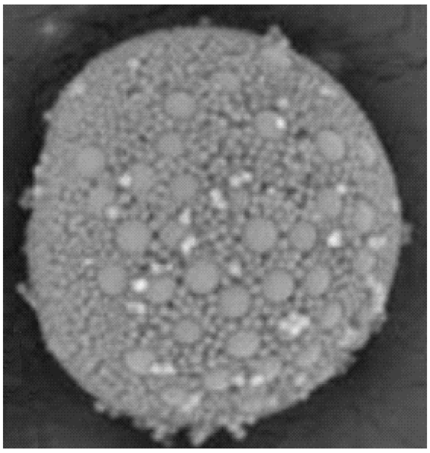

Fig. 3. An example of structurized particle aggregate (size ~ 10 μm) obtained by controlled distribution of primary spray drying of a colloid with bimodal particles (250 nm and 1 μm).

It should be pointed out that some novel inhalation drugs are multicomponent i.e. they form a mixture of two or more active compounds delivered during single inhalation, while the dose of each compound is significantly different (e.g., as 10:1). In such cases the problem of the reproducible delivery of each compound in one dose of inhaled aerosol particles with the desired size distribution becomes much more complex and requires a more thorough analysis [17].

Another strategy to increase the efficiency of inhalation with DPIs is the optimization of aerosol dispersing device (inhaler) to obtain the efficient use of airflow energy (provided by an inhaling patient) for the fluidization and deaggregation of powder particles [18, 19]. CFD analysis and experiments on powders dispersion can be very useful in designing new DPI designs, Fig. 4.

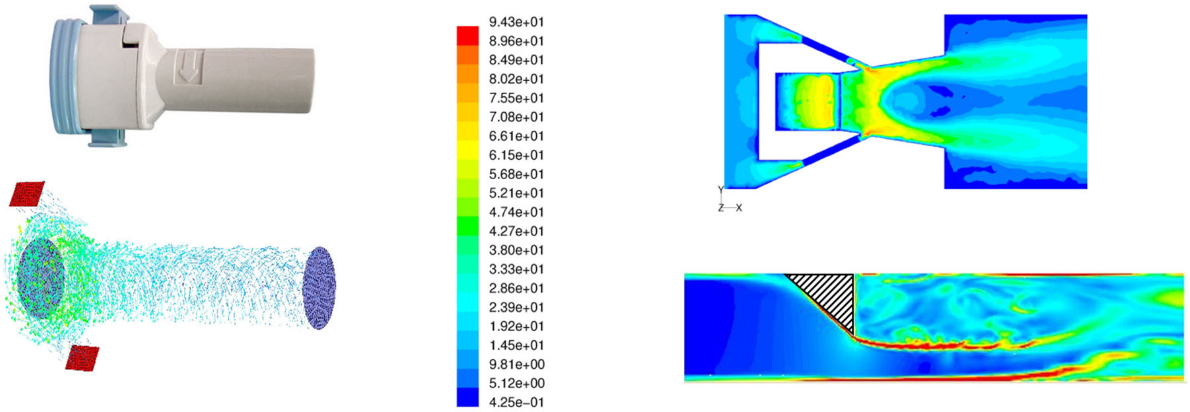

Fig. 4. Examples of use of computational fluid dynamics (CFD) in flow analysis and DPIs design.

Interactions of deposited particles with the lung surface

According to Fig. 2, the important step in achieving therapeutic effect is related to the interactions of inhaled particles with the lung tissue. This process depends on the interfacial processes which occur when particles are deposited on the internal surface of the respiratory tract. The lung fluids: bronchial mucus and pulmonary surfactant are natural barriers which protect the organism against harmful action of inhaled contaminants. It can be shown by rheological and surface tensiometric measurements done in vitro that inhaled micro- and nanoparticles influence the physicochemical properties of both fluids, and that these effects are dose and material dependent [16 and references therein]. Changes in the dynamic surface tension of the pulmonary surfactant have effects on the mass transfer rate in the alveolar region of the lungs, and this may lead to serious health problems [20-22]. This conclusion is important also for inhaled therapeutics which should be designed in a way to avoid undesired physicochemical changes in the pulmonary surfactant properties [15, 23]. The problem has been recently raised also in relation to nebulized drugs which often contain surface-active compounds as preservatives and stabilizers of the liquid formulations [24].

Conclusions

This paper outlines selected problems of aerosol inhalation viewed from the chemical engineer’s perspective. The discussed problem requires incorporation of several aspects of contemporary chemical engineering, such as the physical chemistry and dynamics of colloidal systems, process intensification, micro-/nanotechnology, and bioengineering, and also often it requires the application of modern research tools (CFD modeling, advanced experimental techniques). It has been demonstrated that such approach can be very effective in a better understanding of interactions of inhaled aerosols with the organism, which is important both in toxicology and therapeutic (medical) applications.

Acknowledgment

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Justification of dead zone presence in catalyst pellets.

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Abstract* – *Heterogeneous catalytic processes and biocatalitic processes are the most important types of the processes where existence of zones without reactants were reported. The aim of the work is justification of presence of dead zone in the catalyst pellet by experimental verification of a model solution. Good consistency of theretical and experimental results justify that dead zone is present inside the catalyst pellet.

Keywords – heterogeneous catalysis, dead zone, dead core, effectiveness factor, diffusional resistances

Introduction

Heterogeneous catalytic processes and biocatalitic processes are the most important types of the processes where existence of zones without reactants were reported. And we don't think about physical defects of catalysts resulted mainly from imperfections of manufacturing or activation processes regions of catalysts or biofilms without reactants that arise spontaneously as a result of fast reaction run, despite the fact that in this area catalyst or bio-catalyst (enzyme) could be active. The inactive zone lessens reactor or bioreactor productivity and influences on process economy –it can reduce or even destroy in large scale processes effects obtained in laboratory. For heterogeneous catalysis the zone without reactants was called "dead zone" and it was predicted by Aris[1]. The analytic solution of non-linear problem without external mass transfer limitations and without the dead zone was presented by Mehta and Aris [2] while for the presence of dead zone by York et al. [3]. Szukiewicz [4] extends applicability region of these solutions on the case of important external mass transfer resistances. The aim of the work is justification of presence of dead zone in the catalyst pellet by experimental verification of a model solution.

Results and Discussion

Catalytic micro-reactor (the Microactivity Effi reactor, PID Eng&Tech, Spain) of diameter 9.1 mm equipped with hydrogen generator, was used for investigations. In the reactor was carried out hydrogenation of propylene. As a hydrogenation catalyst the KUB-3 catalyst (the main components of the catalyst are Ni, NiO, and Al_2O_3.) manufactured by INS, Puławy, Poland was chosen. Catalyst form: plate with diameter 4-6 mm and thicknes 0.4 mm. Experiments were carried out at temperature range 100-150°C under pressure 1.2×10^5Pa.

On the basis of experiments carried out the following kinetic equation was developed:

$$r_p = 44400 p_p^{0.5} e^{\frac{-36500}{RT}} \quad [\mathrm{mol/(m^3\,s)}] \tag{1}$$

The kinetic equation indicates that inside the catalyst pellet a dead zone can be formed. Consequently, a mathematical model of the process includes typical mass balance equation with boundary conditions characteristic for dead zone problem [1]. The analytic solution for the problem under consideration is given by:

$$c = \left(\frac{1-n}{2}\sqrt{\frac{2\Phi^2}{1+n}}\right)^{2/(1-n)} (x - x_{dz})^{2/(1-n)} \tag{2}$$

where Φ is Thiele modulus, n is an exponent in the kinetic equation. x_{dz} (coordinate that determines dead zone location) and c_s (surface concentration) can be determined from:

$$1 - x_{dz} = \frac{2}{1-n}\sqrt{\frac{1+n}{2\Phi^2}}\, c_s^{(1-n)/2} \text{and} \sqrt{\frac{2\Phi^2}{1+n}}\, c_s^{(1+n)/2} = Bi_m(1 - c_s) \qquad (3)$$

Effectiveness factor is given by

$$\eta = \sqrt{\frac{2c_s^{1+n}}{(1+n)\Phi^2}} \qquad (4)$$

Effectiveness factor values calculated theoretically and determined from experiment were compared. Results are presented in Table 1. The calculated and determined experimentally values of effectivess factor have close values. The error does not exceed 10% (with one exception – E9) so consistency of results can be treated as good. Determined size of dead zone was about 75%, so a greater part of catalyst pellet remains inactive.

Table 1

Experimental and theoretical values of effectiveness factor

Exp. number	Molar ratio	Temp. [°C]	$D_{ef}\cdot 10^7$ [m^2/s]	k_g	η_{exp}	η_{calc}
E1	0.10	101.4	2.95	0.178	0.0709	0.0780
E2	0.14	111.2	3.58	0.210	0.0669	0.0828
E3	0.12	111.3	3.58	0.196	0.0759	0.0794
E4	0.14	120.3	3.81	0.214	0.0856	0.0765
E5	0.16	120.0	3.81	0.228	0.0840	0.0796
E6	0.20	130.0	3.73	0.424	0.0840	0.0752
E7	0.14	142.0	3.79	0.275	0.0919	0.0925
E8	0.20	141.5	3.79	0.327	0.0986	0.1024
E9	0.20	151.0	3.94	0.439	0.0758	0.0618

Conclusion

Good consistency of theretical and experimental results justify that dead zone is present inside the catalyst pellet since presented in References regular and dead zone model are complementary.

Acknowledgments

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Prediction of the biological activity of naphthoquinone N-derivatives on the basis of virtual screening and drug-like characteristics

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Abstract – The predicted screening of the biological activity of aminopyrazole derivatives dichloronaphtoquinone with the use of the PASS program was carried out and their acute-looking characteristics were determined. On the basis of virtual screening data, perspective directions of experimental biological research of heterocyclic N-derivatives of 1,4-dichloronaphtoquinone were revealed.

Keywords - naphtoquinone, amines, pyrazole, drug-like characteristics, Lipinski's parameters, PASS Online.

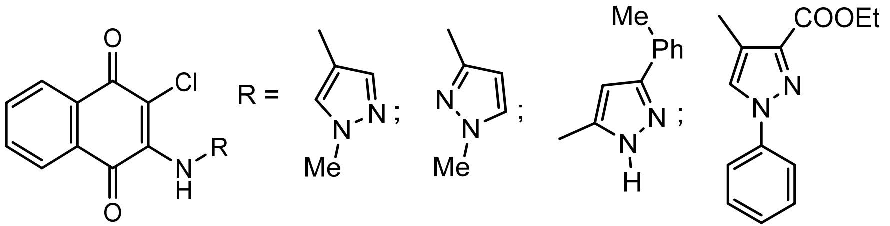
Introduction

The work on the implementation of new drugs is extremely diligent and costly. Therefore, at the initial stage for the search of pharmacologically active compounds, it is advisable to use pre-experimental methods of the virtual screening *in silico* that precede experimental methods *in vitro* and *in vivo*. Such areas of virtual screening in the search of new potential candidates for a drug substance are the use of drug-like characteristics and the prediction of compounds biological activity using the computer program PASS.

For modern pharmacology, the relationship between biological activity and the structure of chemical substances, as well as on their basis the search of new highly active drug compounds has the fundamental importance. It is known that naphthoquinone N-derivatives are potential biologically active compounds with a wide spectrum of action [1]. Therefore, we chose them for experimental purposes.

Discussion of results

As subjects of research, we chose such aminopyrazole derivatives of naphthoquinone:



1a-1d **a** **b** **c** **d**

For planning the directions of experimental research on the biological activity of aminopyrazole derivatives of naphthoquinone, we used the previous computer prediction by the program PASS (Prestance of Activity Spectra for Substances) [2, 3].

After analyzing the results on the screening of the biological activity of aminopyrazoles with the quinone fragment, obtained by the PASS program, the perspective directions of their experimental biological researches were determined, namely: antitumor activity, analgesic, antiparkinsonian, anti-neurodegenerative activity, activity against diabetic neuropathy, as well as the possibility of their use as inhibitors of many enzymes.

Also, an important informative method of prediction is the drug-like characteristics. Using the Internet service [4], which offers a software package for processing introduced structures and property calculations, the Lipinski's criteria have been calculated, and it has been determined that heterocyclic naphthoquinone derivatives (1a-1d) have no deviations from the Lipinski's rules. And, consequently, it is advisable to carry out further experimental biological studies of synthesized compounds (1a-1d).

Table 1

The value of the drug-likeness criteria for 1,4-naphthoquinone N-heterocyclic derivatives

Number of compound	Log P	Molecular polar surface, Å2	Number of non-hydrogen atoms	Molecular weight	Number of hydrogen bond acceptors (O and N atoms)	Number of hydrogen bond donors (NH and OH groups)	Number of rotating bonds	Molecular volume, Å3
1a	2.57	63.99	20	287.71	5	1	2	233.70
1b	2.77	63.99	20	287.71	5	1	2	233.70
1c	4.82	74,85	26	363.80	5	2	3	304.73
1d	4.49	90.30	30	421.84	7	1	6	349.88

Conclusions

The calculation of drug-likeness criteria and predictive screening of biological activity using the PASS program for synthesized compounds have been carried out and the promising N-derivatives of naphthoquinone as potential drug substances have been identified.

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Modeling of intermolecular interactions between epoxyamine grid and hydroxide of metals

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Abstract* - *The method of quantum-chemical modeling investigates intermolecular interactions between epoxyamine grid and hydroxides of metals of various chemical nature. It was established that the influence of hydroxide on the structure and spatial conformation of the grid depends on the acid-base properties and increases with increasing alkalinity of the hydroxide. It is shown that for certain an alkaline property of hydroxide, due to strong intermolecular interactions, the spatial conformation of the grid is significantly changed.

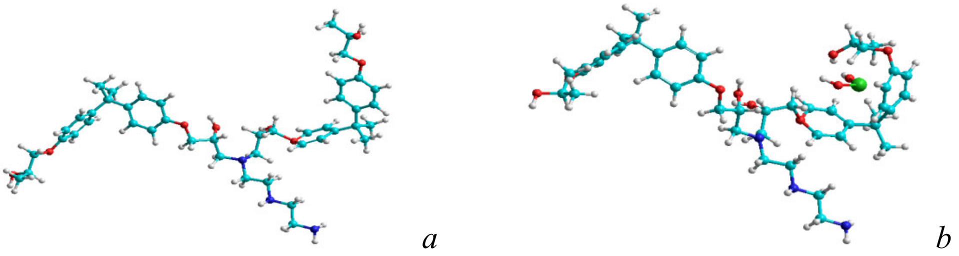
Keywords - epoxyamine grid, metal hydroxide, intermolecular interactions, acid-base properties

Introduction

Disperse oxides and metal hydroxides are successfully used as fillers to produce composite materials based on epoxyamine polymers. The properties of filled epoxy materials depend to a large extent on intermolecular interactions on the phase separation surface. It is known that on the surface of disperse-dry fillers due to adsorption of water molecules a hydroxyl-hydrated layer is formed, represented by hydroxyl groups with different acidity. Surface hydroxyl groups interact with epoxy polymer, which significantly affects the technological, physic-chemical, protective and other properties of composite materials. Therefore, the study of the patterns of intermolecular interactions between the epoxy grid and metal hydroxides is necessary in terms of directional regulation and prediction of the properties of composite polymeric materials.

Results of simulation of molecular complexes

To simulate the interactions between epoxyamine grid polymer and hydroxides of metals of different chemical nature, a fragment of a grid formed as a result of the crosslinking of two molecules of the epoxydian oligomer brand ED-20 and one of the molecule of the diethylenetriamine brand DETA has been used. The investigated molecular complexes consisted of a grid fragment (EP) and a metal hydroxide metals $Al(OH)_3$, $Fe(OH)_3$, $Ti(OH)_4$, $Ca(OH)_2$. In fig. 1 shows three-dimensional models of a fragment of epoxyamin grid and molecular complexes constructed with the help of the HyperChem software package with geometric optimization function.



a *b*

Fig. 1. 3-D models of: *a* – fragment of epoxyamine grid EP, *b* – molecular complex EP+$Ca(OH)_2$, with conditional designations of atoms ● – C; ● – O; ● –H; ● – N; ● – Ca.

As a result of modeling, we obtained the values of intermolecular distance and dipole moments (μ) of molecules and molecular complexes, enthalpy formation (ΔH_{form}) and energy of interaction (E_{int}) of molecules in the complexes.

Calculation results are shown in Table 1.

Table 1

Energy and dimensional parameters of molecules and molecular complexes

Complex	ΔH_{form}, kJ/mol	E_{int}, kJ/mol	Distance between molecules, Å	Dipole moment, μ, D
Fragment of grid (EP)	−1,522.4	−	−	6.15
$Ti(OH)_4$	−1,170.7	−	−	0.15
$EP+Ti(OH)_4$	−1,931.8	181.9	5.9	6.20
$Ca(OH)_2$	−872.3	−	−	0.07
$EP+Ca(OH)_2$	−3,603.6	−288.7	1.7–2.5	4.50
$Al(OH)_3$	−949.1	−	−	2.37
$EP+Al(OH)_3$	−1,710.1	181.9	5.6	8.14
$Fe(OH)_3$	−1,515.0	−	−	3.18
$EP+Fe(OH)_3$	−2,276.3	181.8	3.2–3.9	9.08

As a result of quantum-chemical modeling with the use of HyperChem software package, the following energy and dimensional parameters of molecules and molecular complexes were obtained. Selected systems give an idea of possible intermolecular interactions and formation of non-covalent bonds on the surface of separation of phases in epoxyamine polymer composites [1].

As Fig. 1*a* of the model shows, a fragment of the epoxyamine grid is rather non-symmetrical and has a spatial configuration of a high dipole moment μ=6.15 D. The rest of the molecule of diethylegridriamine is located between residues of ED-20 molecules that repel. Obviously, the residues of ED-20 molecules, which contain benzene rings with delocalized π-bond, repel from nitrogen atoms of DETA residue. By comparing resulting energy and dimensional parameters of the molecular complexes between EP and hydroxides of metals of different chemical nature, it is necessary to note significant influence of the nature of metal (Table 1). Molecular complexes with dipole moment, which is more than μ of individual molecules, are formed at interaction in most cases. Thus, dipole moment of complex $EP+Fe(OH)_3$ (μ=9.08 D) is 1.5 times as high as dipole moment of EP (μ=6.15 D) and 3 times as high as dipole moment of $Fe(OH)_2$ (μ=3.18 D). Dipole moments of complexes $EP+Ti(OH)_4$ and $EP+ Al(OH)_3$ exceed μ of source molecules as well. In the case of $EP+Ca(OH)_2$, on the contrary, dipole moment of the complex (μ=4.50 D) is by 1.4 times less than dipole moment of EP, but by 2 orders of magnitude larger than μ of $Ca(OH)_2$. Obviously, it is connected with the fact that compared with metals of amphoteric nature (Ti, Fe, Al), Ca is strong alkaline-earth. It is characteristic that in this complex the distance between molecules is the least (1.7−2.5 Å), and interactions are the strongest (E_{int}=− 288.7 kJ/mol). This is due to the fact that a molecule of $Ca(OH)_2$ interacts with EP by a fundamentally different mechanism from hydroxides $Ti(OH)_4$, $Al(OH)_3$ and $Fe(OH)_3$. Thus, Fig. 1*b* shows that existence of a $Ca(OH)_2$ molecule causes a change in special conformation of the grid's fragment. Calcium atom is oriented to π-electron cloud of benzene ring with formation of donor-acceptor bond. At the same time, OH-groups of calcium hydroxide form hydrogen bonds with OH-groups of the residue of a ED-20 molecule. This conclusion follows from the values of the measured distance between a $Ca(OH)_2$ molecule and EP, which are compared to the length of hydrogen bond, equal to about 3 Å. In general, it should be noted that calcium hydroxide has the greatest influence on spatial conformation of epoxyamine fragment and causes substantial changes in all energy and dimensional parameters of the grid. As a result of geometric optimization of molecular complexes, it was established that hydroxides $Ti(OH)_4$, $Al(OH)_3$ and $Fe(OH)_3$ are oriented by hydroxyl groups to OH-groups of the grid's fragment. They are located on the opposite side from the residue of a diethanolamine molecule. Location like this is, obviously, the most energy- and spatially conditioned by conformation. The values of enthalpies of formation of the studied molecules and molecular complexes are negative (Table 1). Absolute values of ΔH_{form} complexes are by 1.5–4 times higher than ΔH_{form} of separate molecules. In other words, intermolecular interactions between the studied molecules are energetically predefined. At the same time, obtained results of modeling make it possible to argue that interactions between the hydroxides of amphoteric metals and epoxyamine grid are weak and low-energy. The distances between EP and metal hydroxides are small (3.2–5.9 Å) and are comparable with the distance, which are characteristic for formation of a hydrogen bond (about 3 Å). Energy of interaction of hydroxides $Ti(OH)_4$, $Al(OH)_3$ i $Fe(OH)_3$ and EP grid fragment have close values at different distances between molecules in complexes. Small values of energies of interaction at sufficiently high values of dipole moments (μ=6.20–9.08 D) indicate formation of low-energy inductive and, possibly, dipole-dipole (orientationally) intermolecular interactions. The obtained data show that existence of amphoteric hydroxides does not cause a change in spatial conformation of the EP fragment. From results of quantum-chemical modeling, it follows that ability of metal hydroxides affect the conformation of a fragment of the epoxyamine grid increases in the series: $Ti(OH)_3<Al(OH)_3<Fe(OH)_3<Ca(OH)_2$. This series coincides with the series, in which basic properties increase (acidic properties weaken) of the active Branstad centers (OH-groups) with the central elements: $Ti^{4+}<Al^{3+}<Fe^{3+}<Ca^{2+}$ [2].

Conclusion

Thus, as a result of quantum-chemical modeling, it was found that the influence of the hydroxide of metal on the structure and spatial conformation of epoxyamine grid depends on the acidic-basic properties and increases at an increase of basic (alkaline) properties of an hydroxide due to strong intermolecular interactions (formation of hydrogen and donor-acceptor bonds), the spatial conformation of epoxyamine grid changes significantly. It was shown that between OH-groups of hydroxides of amphoteric nature and the epoxyamine grid, weak low-energy bonds of orientation and induction character are formed. In this case, spatial conformation of the grid's fragment does not change. In general, we can conclude that the nature and energy of intermolecular bonds, which affect the structure of epoxyamine polymer composites, are determined by acidic-basic properties and the chemical nature of the hydroxide of metal.

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New Processes for Cleaning Gas Emissions from Nitrogen Oxides

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Abstract* – The process of cleaning exhaust gases from nitrogen oxides with a solution of carbamide has been examined. Neutral nitrogen, carbon dioxide and ammonium nitrate solution as a fertilizer are formed as a result of the purification. The mechanism of reactive absorption of nitrogen oxides with a solution of carbamide is investigated. The effect of nitrogen oxides concentration, solution temperature, gas flow rate on the degree of purification is shown.

Keywords – simulation, gas purification, reactive absorption, nitrogen oxides, carbamide, absorption column.

Introduction

Among absorption-reduction methods of gas purification from nitrogen oxides, the method involving solution of carbamide is of primary interest. Using this absorbent, nitrogen oxides are deoxidised to ecologically safe elementary nitrogen. Ammonium salts are accumulated in the solution, and they are easily utilised as nitrogen-containing manures. The degree of absorption of nitrogen oxides by the carbamide absorbent at the single stage of absorption reaches 75-80%. This allows synthesising the technological scheme of purification of industrial waste gases that ensures maximally allowable concentration of NO_x in gas exhausts [1,2].

Absorption by carbamide

Carbamide and its solution are highly perspective nitrogen oxide absorbent. When absorption by carbamide solution is used, non-toxic products, such as N_2, CO_2, H_2O, form. The study of the process of gas purification from nitrogen oxides by solutions of carbamide was fulfilled by means of the dynamic method in a glass column with irrigated walls.

To coat all surface of the pipe by a liquid film, the spraying density was at the level of 20 $m^3/(m^2\ hr)$. The process was studied under the following technological conditions: nitrous gas oxidability of 20…60 vol%, air-gas stream linear velocity of 0.5…2.5 m/s, carbamide concentration in absorber of 1…10 %, carbamide solution temperature of 293…333 K, nitrous gas concentration of 0.03…1.0 vol%.

Based on the obtained results, the authors made a supposition that the process is described by the following total equation:

$$NO_2 + NO + 2(NH_2)_2CO + 2HNO_3 \rightarrow 2CO_2 + 2N_2 + 2NH_4NO_3 + H_2O$$

The following stages of the process have been defined by means of the investigations on the process of reduction of nitrogen oxides by water solutions of carbamide:

Nitrogen oxides dissolve in water with formation of nitric and nitrous acids.

Nitric and nitrous acids react partially with carbamide:

$$(NH_2)_2CO + HNO_3 + HNO_2 \rightleftarrows NH_4NO_3 + N_2 + CO_2 + H_2O$$

The supposed mechanism is as follows:

$$HNO_2 + H^+ \rightarrow NO^+ + H_2O$$
$$(NH_2)_2CO + NO^+ \rightarrow CO_2 + N_2 + NH_4^+$$

The second stage is limiting.

To determine the mass-transfer coefficients some experiments were conducted on a pilot plant of the waste gas treating for a glasswork. The column of 0.5 m in diameter consists of the water lock of 0.8 m in height, the layer of regular packing of 1.4 m in height. The gas linear velocity was held at the range from 0.4 up to 2.5 m/s, the spraying density – from 20 up to 40 $m^3/(m^2hr)$. At the spraying density of 28.7 $m^3/(m^2hr)$ under increase of the gas linear velocity from 0.47 up to 2.39 m/s a mass-transfer coefficient of nitrogen oxides absorption by 2% carbamide solution changes in a range of (1.01…2.27) 10^{-10} $g/(m^2 s Pa)$.

Nitrous gases with the oxidation degree less than 50% should be acidified, or it is necessary to use absorbents with a supplement of reagents, which are able to oxidise NO to NO_2. Such reagents are H_2O_2, $KClO_4$, $KMnO_4$.

Conclusion

The obtained outcomes on the NO_x recovery degree dependence on nitrous gas oxidability at the gas linear velocity of 0.5 m/s, the spraying density of 20 $m^3/(m^2hr)$ and 5% carbamide concentration in absorbing solution demonstrate that when oxidability increases from 10 up to 65%, the recovery degree raises from 14.2 up to 53%.

The absorbent temperature increase (under the same absorption conditions) results in the decrease of NO_x recovery degree from 50 % at 283 K up to 14.5 % at 343 K.

When the carbamide concentration increases from 1 up to 2%, the NO_x recovery degree grows from 38.2 up to 45.5%. More than 2% carbamide concentration in the absorbing solution practically does not influence on the recovery degree. For example, the absorption by 5% solution of carbamide augments the recovery degree up to 48.5% only.

The increase of the gas velocity from 0.1 up to 2.5 m/s augments the degree of NO_x recovery from 28 up to 76%.

It was determined that the degree of NO_x recovery depends on their concentration in a gas a little. The influencing is essential at very low NO_x concentrations only. So at 1 vol% of NO_x concentration the degree of recovery makes 85%, and at 0.039 vol% reduces up to 73% (under the same conditions of the process).

It is evidenced that the basic resistance of mass transfer is focused in a gas phase at the low concentrations.

The analysis of the outcomes shows that as the gas mixture linear velocity increases from 1.0 to 2.5 m/s, the NOx reduction degree rises appreciably up to 80% (what allows reaching the required standards for the maximum allowed exhausts of NO for steam power plants – 200 mg/m3). The further rise of the gas linear velocity (more than 2.5 m/s), under the same optimum technological parameters of the process, increases a mass-transfer coefficient slightly up to 82…84%. The needed increase of a gas-air flow linear velocity is limited by both large volumes of power plant exhaust gases and flooding of a column.

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Granulation and drying of fertilizers based on alternative source of phosphorus

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Abstract – The effect of process variables on granulation of fertilizers was studied. Computer simulations of the granulation process were performed. A comparison of application of pan granulator and fluidized bed granulator was presented. The kinetics of granule drying was also determined.

Keywords – granulation, drying, fertilizers, process simulation.

Investigation of the granulation of fertilizers

The amount of organic waste from meat production is growing in the world. The growing amount of bone remains has been recognized as one of the significant environmental challenges. Some of this waste can be reused as fertilizers [1-3].

The properties of powders are of critical where the design and operation of industrial equipment, as well as avoiding problems such as arcing in silos, segregation in solids and other problems that often result in process stoppage or low-quality products [4]. Granulation is one of the methods of improving the fluidity of powders and is done by creating intermolecular bonds between primary particles [1].

Granulation tests were carried out using a laboratory pan granulator and a fluidized bed granulator (Figures 1-3). The materials used for laboratory tests were powdered mixtures of various salts used as components of fertilizers, as well as powdered organic materials and burnt bones. The size of the particles of powdered feed was under 150 µm. Water and aqueous solutions with different additives were used as binding liquid.

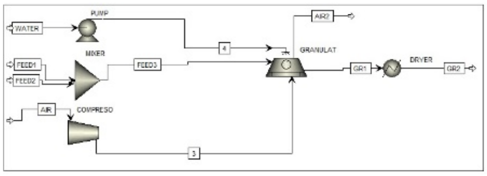

Fig. 1. Granulation process diagram.

Fig. 2. Laboratory pan granulator.

Fig. 3. Fluidized bed granulator.

The aim of the laboratory tests was the selection of the granulation parameters. The influence of the moisture content and encapsulation on the size of granules was investigated using both granulation methods. A mathematical model of the granulation process was developed to support the process design.

The moisture content of the granules as well as encapsulation have significant effect on the granule size distribution (GSD). Figure 4A shows GSD for the fertilizer granulated with the encapsulation, and Figure 4B without the encapsulation. In the former case much smaller granules were obtained. There is no significant difference in GSD obtained with the pan granulator and the fluidized bed granulator (Fig. 5). However, the fluidized granulation requires more binding liquid, and the obtained granules had more irregular shape.

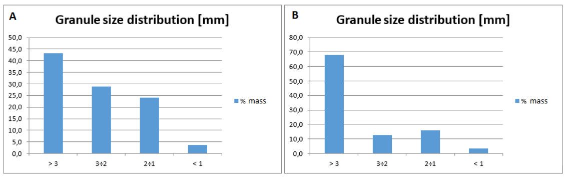

Fig. 4. GSD – pan granulator for: A) with encapsulation; b) without encapsulation.

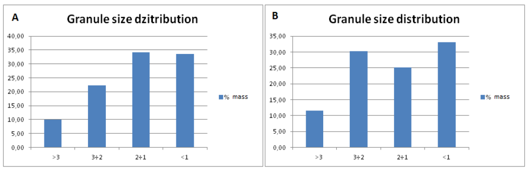

Fig. 5. Granule size distribution for: A) pan granulator; B) fluidized bed granulator.

Investigation of the kinetics of granule drying

The drying kinetics is presented in the form of a drying rate curve. From the obtained data the kinetic time of drying was calculated, which determines the longitudinal dimension of the dryer.

The kinetics of drying for granules with different dimensions of all granulated fertilizers were investigated. The studies performed revealed that practically for all tested granules drying occurs in the second drying period (Fig.6). The total drying times were calculated and compared to the experimental ones. The results obtained were producible, the calculated drying times were in agreement with experimental ones; a relative error between the simulations and the experiments was equal to 1.8-3.6%.

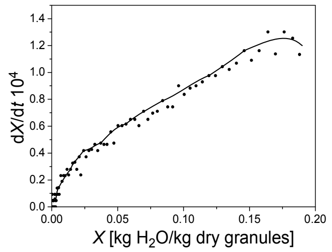

Fig. 6. Representative kinetic curve of drying.

Conclusion

1. The granulation parameters has been selected correctly. Computer simulations of granulation were in agreement with the experimental results.
2. Determination of the drying kinetics of granules of the fertilizers enabled the selection of a dryer type and its engineering design.

Acknowledgments

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The correlation of experimental results for condensation of steam from its mixture with air in channel of plate heat exchanger based on mathematical modelling

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Abstract* – *The process of steam condensation in the presence of air in channels of plate heat exchanger is investigated experimentall and with mathematical modelling. The equation accounting for transvers mass flux on heat and mass transfer is obtained. The results allow design of platecondenserss for steam containing noncodensable gas.

Keywords – heat transfer, mass transfer, condensarion, steam-gas mixture, mathematical model, experiment

A considerable amount of energy consumed in industry is lost as waste heat to the environment. The substantial quantities of this is latent heat of condensable vapours leaving out in the mixture of gases exhausting after burning of fuels, after processes of drying different materials and other exhaust gases from the industry. For efficient utilization of the heat in all such cases there is a need in effective heat transfer equipment which is capable to perform required duty in effective and economical way. Plate heat exchanger (PHE), as one of the modern efficient types of compact heat exchangers, is a good choice for this purpose. However the methods developed for their design with single phase flows [1] cannot be used in case of condensation in one of the heat exchanging streams.

The experiments for condensation of steam – air mixture in a sample of PHE channel were performed. The experimental model consisted of four plates welded together to form three inter plate channels. The channel parts on the gas - steam side were formed by combination of two pates with corrugation angle $\beta = 60°$. The saturated steam-air mixture was directed and condensed in the central channel. It was cooled by water flow in two periphery channels having thermally insulation on the outside. The temperature measuring points are situated at the inlet and exit of heat exchanging streams and at seven points along the channel. The pressure of gaseous stream is measured by pressure gauges at the inlet and exit of the channel. The mass flow rate of cooling water and the flow rate of incoming air are measured. The volumetric flow rate of water condensate created in channel was measured by set of measuring vessels and the flow rate of steam is determined by summing the water condensate flow rate with the flow rate of not condensed steam exiting channel and outgoing steam-air mixture at saturation conditions. The channel model is 1 meter long and its width is 0.225 m. The corrugation height is $b = 5$ mm, thickness of the plate is $\delta = 1$ mm, aspect ratio $\gamma = 0.556$ and area increase coefficient $Fx = 1.15$. The experiments included 48 tests with different conditions of gaseous mixture condensation. The absolute pressure was changed in the range from 2.93 to 1.025 bar; the air volume fraction in entering channel mixture was in the range from 2.8 % to 70 %; the local velocity of gaseous stream was in the range from 46 to 4.1 m/s; the temperature of gaseous stream changed in the range from 88.2 to 115.1 ºC; the temperature of cooling media varied from 23.8 to 71.5 ºC.

To correlate the data of experiments with accounting for process local parameters distribution along the heat transfer surface the mathematical model of PHE for condensation of gas-vapor mixture is developed. The different available models for transvers mass flux influence on heat and mass transfer during condensation of steam from its mixture with noncondensable gas are checked by experimental data. As a base is taken analogy of momentum, heat and mass transfer discussed for PHE channels in paper [2]. The comparison with integral experimental results allowed to select the most reliable physical models of local processes. The model is implemented as software for PC. The estimation is made on the base of calculations of root-mean-square error for 62 experiments. The calculations with the model proposed for straight tubes in paper [3] have shown good accuracy at relatively small intensity of condensation process at volumetric concentrations of air in its incoming mixture with steam more than 50%. The root-mean-square error of calculated outlet temperature of gas-steam mixture for these experiments was 1.8 ºC. However smaller air content and high transverse mass fluxes the root-mean-square error is about 7 ºC with absolute error in some experiments up to 15 ºC. It required the introduction of the additional parameters accounting for transverse mass flux proposed for the use in PHE channels in paper [4] for heat transfer b_H and for mass transfer b_D :

$$b_H = \frac{c_s}{c_{mx}} \cdot \frac{J_s}{\rho_{mx} \cdot w_{mx} \cdot St_H^0}; b_D = \cdot \frac{J_s}{\rho_{mx} \cdot w_{mx} \cdot St_D^0} \qquad (1)$$

where J_s is steam flux to condensation surface, kg/(m^2·s); w_{mx} is velocity of gas-steam mixture, m/s; c_s and c_{mx} are specific heat capacities of steam and gas-steam mixture, J/(kg·K); St_H^0 and St_D^0 are heat transfer and mass transfer Stanton numbers calculated without the influence of transverse mass flux by heat and mass transfer analogy.

With introduction of parameters determined by Eq. (1) and adjusting coefficients with minimization of root-mean-square error the following correlations are obtained for heat transfer *(H)* and mass transfer *(D)* Stanton numbers in conditions of transvers mass flux:

$$St_{H(D)} = St_{H(D)}^0 \cdot \ln\left(1 + \frac{C_{sb} - C_{sf}}{1 - C_{sf}}\right) \cdot \left(\frac{C_{sb} - C_{sf}}{1 - C_{sf}}\right)^{-1} \cdot \left(1 + 1.9 \cdot b_{H(D)}\right) \qquad (2)$$

where C_{sb} and C_{sf} are mass fractions of steam at flow bulk and at condensate film surface.

The results of calculations with the developed model using Eq. (2) are compared with all experimental data. The root-mean-square error is 1.8 ºC for outlet temperature of gas-steam mixture and 2 % for total heat transfer load. It confirms the model validity and accuracy of Eq. (2) acceptable for design of PHEs in industrial applications.

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Molecular modeling using Molecular Dynamics and Coarse-grained models of hydrogel structural and transport properties

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***Abstract* – Natural hydrogels are a specific group of functional materials, that are gaining more and more applicability in various fields. The most important ones include: medicine, tissue engineering, pharmacy, diagnostics, food industry, cosmetics as well as gardening and agriculture. In the study we show state-of-the-art molecular dynamics calculations of gelatine matrices and present methodology of relating the chemical comoposition of such structures with swelling, transport and mechanical properties.**

Keywords – hydrogel, gelatin, molecular dynamics, solubility, diffusion, young moduli.

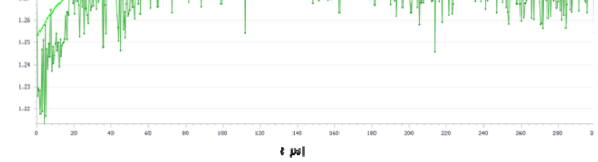
Introduction

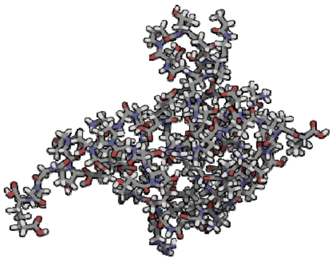
Gelatine is an important material having variety of applications in separation processes, enzyme immobilisation and biomedical industry [1]. Its mechanical, transport and adsorption properties depends on many factors such as water swelling degree, crosslinking degree or temperature. The understanding of the functional dependence between aforementioned parameters-properties has crucial impact on the design and application of given hydrogel matrix. So far investigations were concentrating on experimental approach with only a few of theoretical research [2].

In our work we use state-of-the art multiscale modelling [2] technique that allows to study the properties of the given hydrogel matrix (gelatine) as a function of its atomic composition and contribution of specific atomic coupling the overall free energy.

Experimental Results and Discussion

We present the scheme for creating reliable gelatine molecular models from existing collagen models in PDB data base. In our approach the model of existing collagen is being reduced to a single fiber. Then we sample the regions of of the siber so its composition is statistically complement with the statistics of specific aminoacids in experimental gelatine. Using Monte Carlo technique and Boltzmann sampling we crate molecular models of gelatine blends with other polymers such as Polyvinyl alcohol and Alginic acid of given density and composition.





In out approach we intend to explain the swelling properties of the given hydrogel or its blends via using the concept of franctional free volume and Hansen solubility parameter. Using

NPT Molecular Dynamics [2] technique we may track the temporal evolution of given molecular model according to Newtonian dynamics in the given model of couplings between specific atoms. We show that there is realiable correspodance with experimental results and thus may predict how specific chemical scenario affects mechanical, swelling and transport properties of hydrogel matrix. We also present how to greate a coarse-grained models of hydrogels based on Hansen solubility parameter.

We show that using the Interface forcefield the equilibrium density of our model is 1.276 g/cm^3 being in excellent agreement with experimental values. The results agree well with experimental results available in the literature and we provide a detailed comparison of the accuracy of the given forcefields. Furthermore we present a concept for finding a statistical correlation (QSPR – Quantitive Structure-Property Relationship) between given macroscopic properties of the hydrogel system and its atomistic composition.

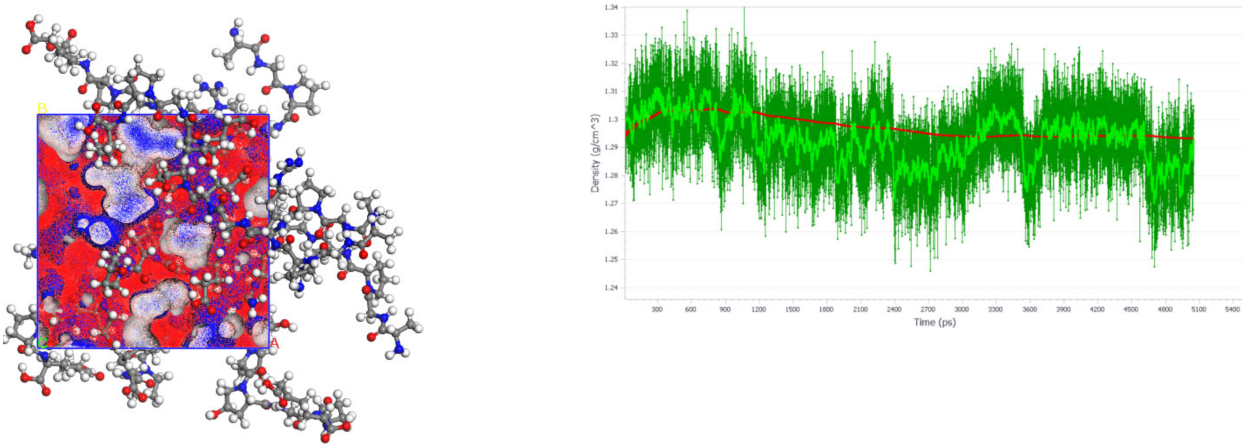


Fig. 1. Left: Gelatine molecular model and fractional free volume visualitzation (blue indicates accessible volume, read inaccessible), Right: density change of gelatine matrix with time in the range of temperatures between 35 and 45 Celcius degree.

Conclusion

The molecular modeling techniques combined with statistical approach gives realiable tool for studying structural, mechanical and transport properties in given hydrogel system Based on on the model we show that the increase in swelling properties with temperature lies directly with the increase of accessible volume within hydrogel matrix.

Acknowledgments

This study was supported by the project “Determination of an influence of composition and spatial structure of hydrogels on the properties of entrapped biocatalysts” financed by NCN 2015/19/D/ST8/01899 (Poland). The computations have been carried out in Wroclaw Networking and Supercomputing Centre WCSS under computational grant no. 172.

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Application of CFD Modeling Techniques to Design and Optimization of Direct-Flow Cyclones

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Abstract* – *In the present study, the direct-flow cyclone model with a varied set of design geometrical parameters has been analysed. Computational fluid dynamic (CFD) tools based on RANS approach and a Eulerian-Lagrangian approach were used to simulate the gas-solid flow in a cyclone separator.

Keywords – direct-flow cyclone, pressure drop, separation efficiency, computational fluid dynamics, numerical modeling.

Introduction

The centrifugal separating method of dusty gases in cyclone separators has been widely used mainly for environmental protection processes in chemical engineering. This type separators of make up from 80 to 90% of the total number of dust treatment plants used in the industry and capture up about 80% of all dust emissions.

At this time, there are many different designs of cyclones. Each of cyclone separator has specific applications and is characterized by appropriate technological characteristics regarding the separation efficiency and energy consumption (pressure drop). Modern engineering research in cyclone design is aimed in two conflicting and simultaneous requirements for minimizing the pressure drop and maximizing the separation efficiency. But it is impossible to implement this approach in traditional counter-flow cyclones design.

An alternative is a transition from traditional counter-flow cyclones design to direct-flow cyclones [1, 2]. This type of separators has already shown its effectiveness, that requires the continuation of scientific and engineering research.

The authors of the study suggest using computational fluid dynamics (CFD) techniques which can represent a viable tool for engineering analysis and design of cyclones. On the basis of numerical simulation and comparison with experimental results, it will obtain a reliable method for calculating gas-dynamic processes and the main parameters necessary for designing direct-flow cyclones.

Experimental Results and Discussion

In this study, the pressure drop, fractional separation efficiency and a flow field in direct-flow cyclone separator were calculated by using a CFD software Ansys Fluent 17. The modeling was performed on a desktop with Intel R CoreTM i5-3230M CPU with 2.60 GHz and 16.00 RAM.

Turbulent gas flow inside the cyclone separator was described by using the Navier –Stokes equations of mass and momentum transport averaged by the Reynolds method (RANS) [3]. This approach is implemented in ANSYS Fluent and requires the additional input of turbulence models. Currently, there is no universal turbulence model for the simulation of all types of flows. Thus, the choice of an adequate model of turbulence creates a serious problem for predicting the basic technical properties of cyclones.

Since the flow in a cyclone is strongly swirled the Reynolds Renormalization Group (RNG) k −ε turbulence model and the Reynolds stress model (RSM) with were selected. Scalable wall functions were employed for near wall treatment. The RNG turbulence model complements with two basic equations such as the equation of kinetic energy of turbulence “k” and that of the rate of energy dissipation “ε”. While the RNG model is a very robust and widely applicable model, it was determined to be less accurate for swirling flow due to the isotropic turbulent viscosity assumption. The RSM model is more accurate for swirling flows and is based on transport equations for all components of the Reynolds stress tensor and the respective dissipation rate. But it should be noted that the RSM model is considerably more computationally intensive [3].

Lagrangian approach with DPM (Discrete Phase Model) was used to calculate the discrete phase motion and to predict the separator efficiency in the cyclone separator. The DPM model takes into account the gravity force of the particle and the coefficient of restitution with the cyclone wall.

The analysis of the gas-solid flow numerical simulation results was performed based on the comparison with experimental data of pressure drop and separation efficiency for a different design of direct-flow cyclon separators. It was found that the differences between the values of pressure drop predicted by CFD simulations and obtained from measurements were small than 5%. However, in the case of separation efficiency simulated results and experimental data were quite different for small particles diameter from 1 to 10 μm. This fact can be explained by accepted assumptions in used models.

Conclusion

The numerical model has been created to understand the effect of the cyclone geometrical parameters on the cyclone separation efficiency and pressure drop values. Based on experimental data and modeling results it was found that the main cause of the low pressure drop values is the direct gas-flow in the cyclone. The new cyclone design results in nearly one-half the pressure drop obtained in the traditional counter-flow cyclones design. The results obtained in this work indicate that these ideas can provide an alternative approach for new design cyclone separator creation.

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Investigation of temperature processes in the process of interaction of technological units and production of products in a machine of bread baking

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Abstract – The technological process is described and the executive devices of the developed bread baking equipment are investigated. An experimental algorithm for heating the molding-baking device was experimentally investigated, established functional temperature dependencies between the matrix and heating punches. Dependence of the deformation (temperature expansion) of the interacting elements of a baking device for different temperature ranges was obtained.

Key words – grain bread, automatic machine, baking, punch, matrix, temperature, pressure.

Introduction

The profound knowledge of modern technologies and patterns of processes that are carried out during the development of food products, allows you to intensify processes, create new types of devices, develop methods for optimal process management [2].

By purpose, processes considered in food technologies, are grouped into four groups: 1 – mechanical; 2 – hydromechanical; 3 – mass exchange; 4 – thermal.

It is the study of the technology of obtaining a quality product, based on the study of thermal processes in the interaction of technological units and the formation of products in the machine baking bread and devoted to the page of this work.

Methodology of conducting an experiment and research results

To obtain reliable results, a methodology for step-by-step experiments was developed:

1. Determination of the coefficients of heat transfer, linear and bulk expansion of contacting elements of the molding-baking device (two plates with punches, heated by shades and a moving matrix that contacts them). The thermoregulators that control the shades are discretely adjusting to the values of specific temperatures at an interval of 20 degrees in the range of 30 ... 50 to 280 degrees. When the specified temperatures reach the pyrometer, the temperature at the control points on the plates of the punches and the matrix is fixed.
2. Since the time of reaching the temperature plate slabs of 280 degrees, the coordinate of the time is fixed and after each 5 minutes the temperature readings of the matrix control points are removed to determine the time of the device's output to the baking mode (approximately 2600). Thus, the parameters of convection of both plates are determined.
3. Repeated actions of item 1, only at control points, not temperature is measured, and linear movement (expansion) of parts of the molding-baking device.
4. When changing the temperature on the thermoregulators, when in the baking mode, at a stabilized time of baking time, they find a range of temperatures, which guarantees a high-quality output.

Means of control

The following measuring instruments were used for the experiment:

- Thermostats Siemens 0 ... 24V; 500 deg .; 0.1; (included in the control panel of an automatic device for controlling the heating of eight tents with a capacity of 1.5 kW each);
- Pyrometer Bosh-300 ... + 600; +/- 2 degrees;
- Digital DT9205A multimeter with thermocouple;
- Indicator lever head КИ-0,01 with a circular scale;

- Gauges 0 ... 250; 0.01;
- Temperature sensors PT-100, $D = 6$ mm.

At the time of taking off the impressions, the ambient temperature in the shop was +25 degrees, humidity was 87%, there were no drafts of air in the area of the machine.

Comparison of results with alternative calculations and visualized results obtained using SolidWorks software showed that they differ in the range of 5% [1].

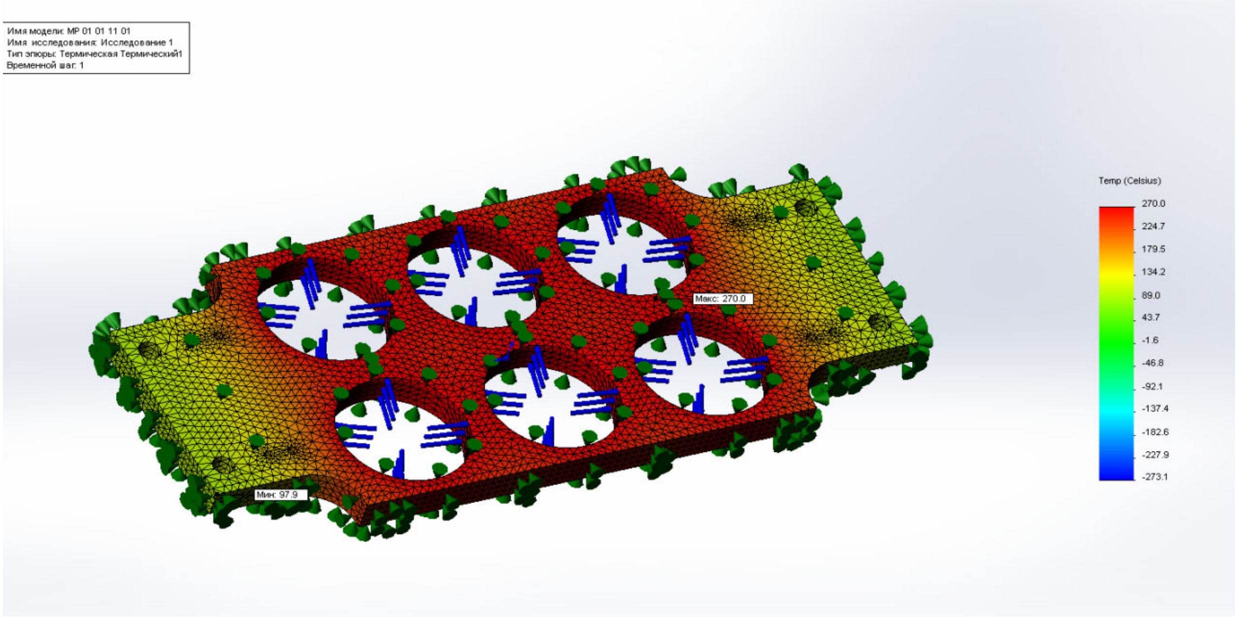

Fig. 1. Visualization of alternative results obtained using SolidWorks software.

Conclusions

1. Experimentally defined algorithm of heating the molding-baking device, to establish functional temperature dependences between the matrix and heating punches;
2. Deformation (temperature expansion) of the interacting elements of the baking device for different temperature ranges is obtained;
3. The range of temperature characteristics of the device, providing the output of a qualitative product, is determined;
4. Determine the dependencies between the force of locking the matrix with punches, the temperature of the heating and the time of baking the product;
5. Determine the optimum performance of the machine, while providing high-quality baking;
6. Compile the results of the experiment with alternative calculations and visualized results using the software SiolidWork.

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Computational Fluid Dynamics (CFD) Study of Mixing and Heating Time Prediction for Two-Components Mixture in the Small-Scale Reactor

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Abstract – The CFD model of mixing and heating process of the two-component reaction mixture in a small-scale reactor is presented. The simulated results have been compared with experimental data and given the opportunity to evaluate the application of the proposed approach to the development and design of large-scale apparatus for the synthesis of allyl-1,3,4-trimethylcyclohex-3-enecarboxylate in industrial conditions.

Keywords – mixing, heating, CFD (Computational fluid dynamics) modeling, sliding mesh, small-scale reactor.

Introduction

The industrial synthesis of many compounds in chemical technology occurs in mixing reactors [1-7]. It is well known, that the hydrodynamics of the mixing has determined the efficiency of the heat and mass transfer of the reaction medium and the kinetics of the chemical reaction. In addition, the physical properties of the original reagents have a strong effect on the efficiency of the process.

In many cases, the mixing is carried out mechanically through having been used various designs of mixers. The experimental research in laboratory conditions which directed at optimizing of the design of stirring mixer device, the geometry of the apparatus, determining the energy consumption for mixing and determining the optimal conditions for conducting of the process, have been often detected ineffective. This is due to the fact, that the energy efficiency and the intensity of mixing are reduced in the transition from laboratory models to industrial plants and at increased the volume of reactive capacity. The holding of the experimental research on an industrial scale is quite expensive and requires considerable time consuming, and in some cases, it may not be feasible at all.

The authors of the study offer being used the methods of computational hydrodynamics, such as an alternative approach. The main advantage of numerical simulation of mixing tasks is the independence from the scale factor. However, one of the main problems arising in numerical simulation of the mixing process is the choice of an adequate model of turbulence and a model that will have been describing the interaction between components of the mixture. With this in mind, it is crucial to verify the results of CFD simulations with the results of a physical experiment to evaluate the mixing process.

Results and Discussion

Mechanical mixing in the reactor volume is a complicated hydrodynamic process that carries out using mechanical stirrers. The mixer which rotates in fluid volume provides fluid by energy, that creates complex circulation flows. Traditionally, the three levels of mixing are distinguished: macroscale, mesoscale and microscale. Each scale is characterized by different vortex structures of streams in the apparatus and has a different nature.

The microscales vortices constantly are changing in size and shape also primarily depending on the pulsating component of the speed, at the same time as the vortex structures of the macro- and mesoscales will have been resistant in size and shape, which respectively complicates the simulation process.

The authors of the study had used the program complex of numerical simulation ANSYS Fluent 17, as an instrument for simulating of the reaction mixture mixing process in the small-scale-reactor. The essence of such an approach, that implemented in ANSYS Fluent, lies in the numerical solution of the basic equations of hydro-dynamics, namely - the equation of continuity, the equation of conservation of the momentum, the energy conservation equation. These equations have expressed a base model of the flow and may be supplemented by equations for modeling turbulence, component transport, chemical reactions, and the like.

The model of the small-scale-reactor in the form of the internal domain was created by the means of 3D modeling ANSYS Design Modeler and is presented in Fig. 1. The diameter of the reactor is 50 mm, the height is 60 mm. The reactor is equipped with a stirrer in the form of a cylinder (rod) with a diameter of 8 mm and a length of 25 mm. The speed of the mixer is makeup 40 rpm.

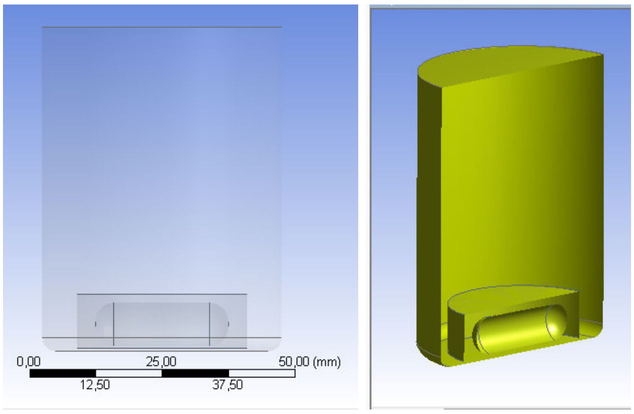

Fig.1. The microreactor geometry.

The authors have used the sliding mesh approach Sliding Mesh for correct modeling effects of interaction between elements and zones, that are moving with different speeds in the small-scale-reactor because in this approach the mesh elements of different zones physically are moving one relative to one another. That’s why, the geometric scale area calculation was divided into two separate domains - the inner domain (internal moving domain) and the outer domain (outer area). In addition, this approach allows us to simulated the mixing process in the non-stationary formulation, which is extremely important in view of the simulation of the chemical interaction between mixture components.

The mesh model, that was used for simulation, had created in the Mesh preprocessor, which contains approximately 500 thousand unstructured tetrahedral elements. It should be noted, that the greatest density of the mesh is concentrated in the area of the mixer, where the highest gradients of speed are observed and near the reactor wall where the heat flux is dominated.

The RANS approach has been used for turbulence modeling. The basic equations of the model were supplemented by k-e RNG, k-e Realizable and k-w SST turbulence models to model the flow behaviour. The simulation of the components interaction was carried out by means of the model Species, as well as the Euler-Euler approach - the mixture model Mixture. The choice of a mixture model has a significant advantage over other models of the Euler-Euler approach in practical application. This model is less resource-intensive, and for homogeneous mixtures and systems similar to them it has been more resistant compared to other models. The physical properties of the mixture components (density, viscosity) are presented in table 1.

Table 1

The physical properties of the mixture components

Compounds	Density, g/cm3	Viscosity, Pa·s
2,3-dimethylbutadiene	0.726	0.0000727
allylmethacrylate	0.9335	0.0006

In the ANSYS Fluent program was implemented the Species model for the simulation of homogeneous mixtures that consist of several components and effectively mix at the molecular level. This approach has also been used for modeling of the mixture behaviour.

The additional boundary conditions on the walls, method of resolution, sampling schemes, properties of the materials, and so on were set up in the process of setting up the ANSYS Fluent solver.

The results are showing the behaviour of the flow and help explain the physical experiment results. According to the presented results, it was installed, that the maximum flow rate is observed in the lower part of the reactor, where the mixer was located. In the device, there are small-scale local stagnation zones, where zones of zero flow have been formed. The fluid is moving in circular trajectories in the mixer zone. The circulatory flows that will have formed at the top of the reactor are causing an increase in the concentration of the solution in the lower part of the reactor. These observations have been clearly agreeing with the results of experimental research performed earlier.

Conclusion

A three-dimensional mixing model of components in a small-scale reactor has been developed using computational fluid dynamics techniques. The rotational movement of the mixer has been modeling on the basis of the Sliding Mesh approach.

The flow model takes into account the availability of two different mixture components and their interactions have based on the Species model, as well as the Euler-Euler approach - the Mixture model.

The presented results have given an opportunity to draw a conclusion, that the developed model will be using to predict the time of non-stationary mixing for the purpose of simulation industrial type machines and optimize technological processes for the synthesis of allyl-1,3,4-trimethylcyclohex-3-enecarboxylate.

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Mathematical modeling of the nonstationary sugar mass crystallization process in the vacuum machine heating tube wall layer

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Abstract – A mathematical modeling of the nonstationary sugar mass crystallization process from the unsteady heat and mass transfer process viewpoint are considered. Sugar massecuite as a cellular model represented. With the simultaneous unsteady heat and diffusion mass transfer problems solution between the system cells were considered variable thermal physics characteristics.

Keywords – mass sucrose crystallization, unstable heat and diffusion mass transfer.

Introduction

The process of mass crystallization of sucrose in the sugar massecuite boiling is the most energy intensive industrial production of sugar. For its control and reduce the energy necessary to create a mathematical model of the process that would fully describe it. It is this and devoted to this work.

Materials and methods

Taking into account all thermophysical, technological and hydrodynamic characteristics when creating a mathematical model of mass crystallization of sucrose is extremely difficult and practically impossible. As a result, a number of simplifications were made. Thus, the mathematical model of the mass crystallization process of sucrose is idealized.

All sucrose mass crystallization processes are considered from the point of view of the non-stationary variable-time heat and mass transfer process. Sugar massecuite was considered in cellular models terms: crystal sugar, which is surrounded by a corresponding volume crystal layer between sucrose solution. Find the simultaneous non-stationary heat transfer problems solution for each cell separately and non-stationary diffusion mass transfer problems between the corresponding intercrystal sucrose solution cells by analytical methods is extremely difficult. In connection with this, at the same time, non-stationary heat conduction problems and non-stationary diffusion mass transfer problems for the intercrystalline sucrose solutions areas by numerical methods were solved.

Results

On the basis of the simultaneous system solution of seven non-stationary heat conduction problems and three separate non-stationary diffusion mass transfer problems, a non-stationary temperature distributions for the entire cells system each component were found. Concentration distributions in the corresponding intercrystal sucrose solution regions were also found for stable and variables of the thermophysical characteristics of the cells of the system.

Conclusion

The received number of different non-stationary temperatures and concentrations distribution in the cells system allows us to determine the more optimal conditions for boiling sugar massecuite a with minimal energy consumption and minimal losses of the finished product.

Molecular dynamics simulation of Ion Beam Etching as technology process for creating graphene-based membranes

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Abstract – Carbon nanomaterials present new possibilities for creating permeable membranes. Ionic beam etching technology allows to create pores in graphene substrates and has the potential to be used in various separation processes. In our study we present a molecular dynamics simulation of the energy needed to puncture the graphene surface to create porous surface. Experimental part shows dependency of irradiation time to pore diameter on silica substrate, which indicates it is possible to create pore diameters lesser than the beam diameter. We present a technology process of creating pores of a specific diameter.

Keywors – graphene, membrane, transport, ion beam, molecular dynamics.

Introduction

According to the definition, a membrane is a "structure, having lateral dimensions much greater than its thickness, through which mass transfer may occur under a variety of driving forces" [1]. Membranes processes can separate particles and molecules and over a wide particle size range and molecular weights. Efficiency in a membrane process is determined by a selectivity parameter. Unique structure of a one atom thick sp^2-bonded carbon sheet of graphene presents unique properties than other forms of carbon in context to membranes. It has large theoretical specific surface area and even with pores its structure remains very resistant to pressure. It has potential for being a material to create very selective and permeable membranes, with personalized pore diameter for various processes e.g. gas separation, electrodialisys, nanofiltration [2]. Functionalizing its surface it further changes the properties of a porous membrane created from graphene sheet. As shown in the MIT computational study, transport of water through nano-porous graphene-oxide membranes could reach up to 66 L/cm2/day/MPa with greater than 99% salt rejection. [3]. Creating a porous surface on a graphene can be carried out by focused ionic beam etching and it is possible to influence the pore diameter with respect to irradiation time and the by choosing an optimum angle [4].

In our work we use classical molecular dynamics code with a focus on materials modeling to develop a technology for creating a technological process for creating porous surface on graphene.

Simulation and experiment

We present the process for creating reliable molecular dynamics model of graphene surface ion beam etching carried out for various pore diameters. In our approach the model of single and several graphene sheets are hit by a fullerene model to imitate the energy density of ion beam. We created a dependency graphs of kinetic energy to pore diameter using several different fullerenes models. To our simulation we used the AIREBO [5] force field potential, which is a good system for modeling carbon and/or hydrogen atom interactions. The deflection of fullerene model indicates that with optimal angle and low enough kinetic energy it is possible to create pores of smaller diameter than the ion beam diameter.

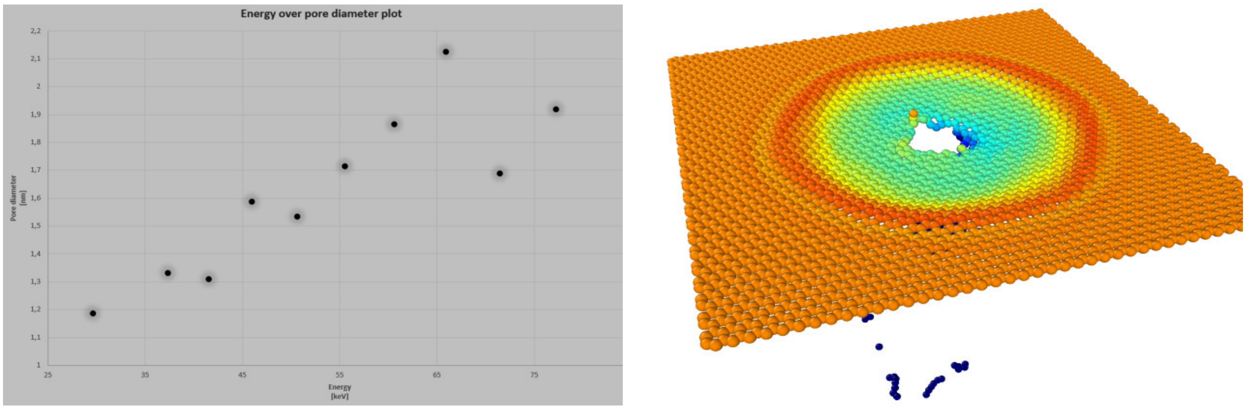

Fig. 1. Left: Dependency of energy density to pore diameter in C180 fullerene model simulation, Right: Graphical representation for the impact simulation in molecular dynamics model created by LAMMPS package [6] with Ovito plugin [7].

Experimental part was to create a dependency of the pore diameter to the irradiation time. It was carried out with ionic beam etching on a silicon substrate.

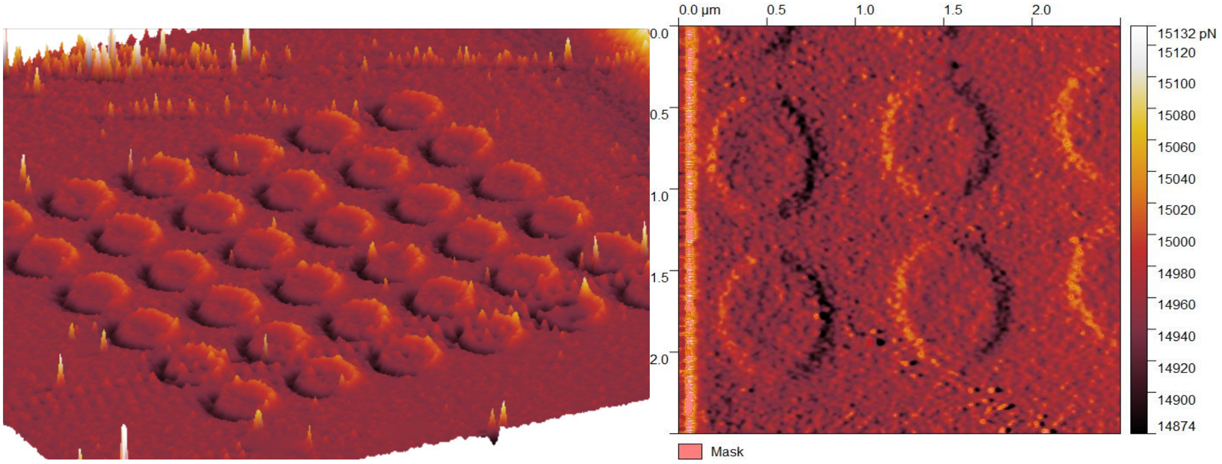

Figure 2. AFM pictures of Silicon substrate after FIB etching done in Nanores company in Wrocław.

Conclusion

The molecular dynamics model can very well be used to imitate the ion beam irradiation on the graphene surface. The characteristics of graphene's response to ion irradiation can be used to gain detailed control over produced defect types. This information is needed in order to controllably create porous membrane from this material, and then to create a experimental installation using this type of molecular sieve.

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

Process Stages Energy Efficiency Increasing In High Capacityammonia Production Plants (1360 – 1420 T NH_3/Day)

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Abstract – There are presented the results of low temperature CO to CO₂ conversion investigations for decreased steam consumption and deeper conversion of CO in nitrogen-hydrogen mixture. The results of monoethanolamine purification stage retrofit are presented too.

Keywords – ammonia plant, nitrogen-hydrogen mixture, conversion, carbon oxide, reaction, equilibrium, reaction rate, energy efficiency, steam.

Introduction

In Ukraine synthetic ammonia is produced by 18 plants with total capacity 6.2 million tons per annum. Total energy consumption is $10 Gcal/tNH_3$ that is 25 % more than energy consumption of similar plants abroad.

Main energy consumer of ammonia plant is the stage of nitrogen-hydrogen mixture preparation from natural gas – methane (CH_4).

The natural gas and energy resources consumption decreasing is actual goal today.

According to ammonia production processing rules in high capacity ammonia plant AM-76 ($1420 tNH_3/day$) steam consumption for ratio $n = V_{H_2O}^{CO}:V_{\text{СГ}}^{CO} = 0{,}44:1$ is significantly more than necessary according to stoichiometric reaction of carbon oxide (II) conversion:

$$CO + H_2O \rightleftarrows CO_2 + H_2 + 41{,}13\,J \qquad (1)$$

Carbon oxide conversion in mixture for decreased steam consumption

To estimate the possibilities of surplus steam decreasing the investigation of kinetic and thermodynamic of CO conversion in nitrogen-hydrogen mixture stream close to industrial was carried out with use of copper contained catalyst K-CO and CHK-2 with particles of catalyst size (0.25-0.5) and (0.1-1.5) mm.

According to the investigation plan the parameters of CO to CO_2 conversion process were varied: temperature, $t°C$, pressure P, MPa, volumetric flow rate $W, 1/hour$. Their influence on equilibrium level of carbon oxide conversion χ_{CO}^* was investigated as well as steam, CO, CO_2 and H_2 containing in the mixture.

The investigations had shown that process temperature t increasing resulted the decreasing of equilibrium level of conversion χ_{CO}^* according to constant of rate K ($molCO/molNH_3$) increasing and from another side in return reaction (1) the equilibrium was removed to initial substances side and χ_{CO}^* was decreased.

Gas mixture pressure $P(MPa)$ increasing from 0.1 to 4.0 MPa causes only small increasing of χ_{CO}^* because of higher inlet concentrations of CO and H_2O in gas mixture.

The most influence to CO conversion process had different ratios «steam-water» $n = V_{H_2O}^{CO}:V_{\text{СГ}}^{CO}$ from (0.1:1) to (0.3:1). For these rates χ_{CO}^* was increased from 0 to $\chi_{CO}^* = 80 - 85\%$. Further increasing $n > (0.3:1)$ not led to significant increasing of equilibrium rate of carbon oxide conversion χ_{CO}^*.

The results obtained show that chemical reaction of carbon oxide (II) conversion has forced mechanism on CO and relates to reducing-oxidizing chemical reaction.

It was proved that kinetic orders of reaction (1) are as follows: hydrogen H_2 not influences on reaction rate r_{CO} ($m_{CO} = 0$); carbon dioxide (IV) decreases the rate of direct reaction ($m_{CO_2} < 0$); carbon oxide proportionally increases reaction rate and has the first order ($m_{CO} = 1$); relating to water the reaction order depends on rate $n = [V_{H_2O}^{CO}]:[V_{CO}]$ and m_{CO} changes from 1 to 0.

It is necessary to notice that increasing of «steam-gas» ratio above $n = V_{H_2O}^{CO}:V_{\text{СГ}}^{CO} > 0.3:1$ has not significant influence on the rate of CO conversion process.

According to obtained results of low temperature CO conversion investigations it is possible to conclude that existing ratio «steam-gas» according to adapted process regulations is equal $n = 0.44:1$ and shows on significant steam surplus in nitrogen-hydrogen mixture.

Kinetic and thermodynamic calculations of low temperature CO conversion with decreased ratio $n = V_{H_2O}^{CO}:V_{\text{СГ}}^{CO} > 0.38:1$ shows on steam consumption saving $G_{\text{П}} = 157.5\, kg/tNH_3$ or energy saving $0.104\, G\, cal/tNH_3$ for ammonia plant AM-76 ($1420tNH_3/day$).

Investigations of deeper carbon dioxide conversion for III-d stage

For final CO removal the metanation process is carrying out according to reaction:

$$CO + 3H_2 = CH_4 + H_2O \tag{2}$$

where the hydrogen necessary for ammonia synthesis is spent. Methane obtained according to reaction (2) is the ballast in nitrogen-hydrogen mixture and is periodically removed with another ballast gases.

To decrease the hydrogen losses according reaction (2) the investigations of deeper conversion of CO to CO_2 were carried out for virtual III-d stage of conversion with input content of CO equal to 0.49 % vol.

The results show on thermodynamic and kinetic possibility of CO conversion on III-d stage at different «steam-gas» ratios $n = V_{H_2O}^{CO}:V_{\text{СГ}}^{CO} = (0.1:1)-(0.5:1)$ at temperature range $t = (180 - 220)°C$ and similarity of process mechanism with low temperature conversion of CO to CO_2 at initial equilibrium concentration $2.9\ \%$ of hydrogen.

Thermodynamic and economical calculations had shown the efficiency of III-d stage unit of deeper conversion for ammonia plant AM-76 ($1420tNH_3/day$) that saves $4\ \%$ of hydrogen consumption that led to increase plant capacity on 60tNH_3/day, and 57 % decreasing of purge gases and therefore connected ammonia losses.

Enhancement of efficiency of monoethanolamine purification stage

The use in ammonia plant the III-d stage of CO conversion increases the content of carbon dioxide (IV) in nitrogen-hydrogen mixture more than normative so it is to be removed with monoethanolamine (MEA) capture stage.

To enhance the efficiency of MEA capture stage the number of scientific investigations and design works were carried out to retrofit this stage at two ammonia plants AM-70 ($1360tNH_3/day$). Existing shell-and tube heat exchangers at position 310 were changed on system with six high effective plate heat exchangers and desorbers as heat recuperators from hot lean solution to cold MEA-solution rich with carbon dioxide (IV) and as partial desorbers of CO_2 before regenerator.

High efficiency of plate heat exchange system let to decrease the temperature difference at hot and cold ends of heat exchange position on $10°C$ and to decrease steam consumption of regenerator reboilers on $7t/hour$. Simultaneously the heat losses through air coolers of lean MEA-solution before absorber inlet and through vapor mixture condenser were decreased on $8.35\ MW/hour$.

Conclusion

The indicators mentioned above may significantly increase the efficiency of existing high capacity ammonia plants and decrease the natural gas consumption.

Conditions for the formation of cavitation

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***Abstract* – Based on analysis of information sources was found that dimensionless complexes - numbers of cavitation, Reynolds, Weber - are used to characterize the intensity of the development of cavitation phenomena. It was established the critical value of the Reynolds criterion (Reqr = 32,500) in the case of the treatment of the aqueous medium in a hydrodynamic jet cavitator, which will enable to regulate the intensity of the development of cavitation and to avoid its negative consequences.**

Keywords – cavitation, simplexes of geometric similarity, number of cavitation, Reynolds number, hydrodynamic jet cavitator.

Introduction

Cavitation is an effective method of intensification of hydromechanical, thermal and mass transfer processes, in particular processes: purification and disinfection of water; disinfection and shelf life in the food industry; purification of diffusion juices and increase of reactivity of slurry lime milk in the sugar industry; reduction of viscosity of petroleum products; receiving nanomaterials, etc. At the same time, the concentration of energy released as a result of the cavitation bubble splashing in small local volumes of the fluid causes the erosion of the surfaces of materials, accompanied by noise, vibration and causes a decrease in the efficiency of the hydro aggregates. That is, it is possible as a useful application of cavitation (innovative cavitation technologies in the chemical and food industries), as well as the emergence of negative effects as a result of cavitation phenomena. Therefore, it is important to analyze the conditions for cavitation and parameters for assessing the intensity of cavitation phenomena.

Parameters of estimation of intensity of development of cavitation phenomena

In accordance with the traditional definitions, "cavitation" is the phenomenon of formation in the liquid of cavities (cavitation cavities, bubbles), which is conditioned by local pressure reduction to the values of pressure of saturated water vapor under the given conditions.

The condition for the formation of cavitation in a liquid is written as follows [1]

$$f\left(\frac{l_1}{l},\ldots,\frac{l_n}{l},k,Re,We\right)=0, \qquad (1)$$

where l, l_1, l_2, …, l_n – linear values that determine the size, shape, location of the working body, the state of its surface, as well as the size of microbubbles and solid particles forming the "core of cavitation"; $\frac{l_1}{l},\ldots,\frac{l_n}{l}$ – simplexes of geometric similarity; k, Re, We – numbers (dimensionless complexes) of cavitation, Reynolds, Weber.

The number of cavitation (k) is the ratio of the pressure difference to the dynamic head

$$k=\frac{2(P-P_{нас})}{\rho w^2}, \qquad (2)$$

where P – pressure in free flow, Pa; $P_{Нас}$ – pressure of saturated water vapor at a certain ambient temperature, Pa; ρ – density of medium, kg/m^3; w – flow rate of liquid, m/s. It characterizes the distribution of cavitation bubbles in technological volume. Depending on the value of k, four types of streams are distinguished: 1) pre-cavitation (k> 1) - continuous (single-phase) flow; 2) cavitation (k≈1) - two-phase flow; 3) film (k <1) - a clear separation of the cavitation cavity from the continuous flow; 4) supercavitational (k << 1). In the case of supercavitation, noise and vibration significantly weaken, and erosion on the local support is practically absent.

The Reynolds and Weber numbers are similarity criteria of hydrodynamic processes that determine the ratio of inertia forces of a fluid to viscosity forces or surface tension, respectively:

$$\mathrm{Re}=\frac{\rho w l}{\eta}, \tag{3}$$

$$\mathrm{We}=\frac{\rho w^2 l}{\sigma}, \tag{4}$$

where η – coefficient of dynamic viscosity of the medium, Pa•s; σ – coefficient of surface tension, N/m. Often, for the characterization of the intensity of cavitation, a set of two dimensionless complexes - numbers of cavitation and Reynolds - are used. Cavitation occurs if $\mathrm{Re}>\mathrm{Re}_{кр}$ ($\mathrm{Re}_{кр}$ is the threshold value of the Reynolds number).

For studies aimed at establishing parameters that correspond to the occurrence of cavitation, a hydrodynamic cavitator of the jet type (HCJT) with a system of profiled nozzles was used. The pressure at the entrance to the cavitator in the range 0,36 ... 0,60 MPa was changed by bypass [2]. Output water temperature is 291 ± 3 K. It was found that for cavitation numbers close to 1, $\mathrm{Re}_{кр}$ = 32 500. In this case, the critical pressure value is 0.47 MPa. A photo of the cavitation area in the HCJT is shown in Fig.

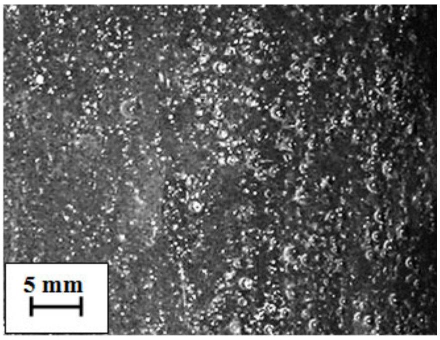

Fig. Photo of the cavitation area in the HCJT.

Conclusions

Establishing the critical value of the Reynolds criterion will allow to regulate the intensity of the development of cavitation and minimize its negative consequences.

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Determination of heat of evaporation of soy-carrot mixture

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Abstract* – *Thermal effect - one of the most widespread heat-engineering operations in the processes of processing of plant raw materials. in the process of drying vegetable raw materials a lot of energy is spent on the evaporation of moisture. The practice of drying a series of complex plant materials indicates a significant difference in the actual values of heat consumption to evaporate from them the moisture from the heat of evaporation of pure water.

Keywords – specific heat of evaporation, moisture, heat-transfer, mass-transfer, drying.

Introduction

The main problem of drying whole soybeans is maximal preservation of phytoestrogens and prevention of oxidation of its lipids [1,2]. Growth of energy costs when drying vegetable materials is associated with difficult permeability of cell membranes for water and the difficulty of removing water that interacts with the soluble components of cellular juice and skeletal material of the material. Consequently, it is important to investigate the effect of creating functional compositions of plant material on the specific heat of its evaporation [3]. To determination of the heat consumption for evaporation of moisture from the proposed functional mixtures, a specific heat of evaporation of water from them and their components was investigated.

The calorimetric method was used, based on the continuous simultaneous measurement of the mass loss of the sample and the amount of heat expended on the evaporation of moisture during isothermal drying. Experiments were carried out with the help of the improved version created in IETP NAS of Ukraine synchronous thermal analysis installations DMKI-01, where a calorimetric platform with deep cylindrical cells is used that allows to investigate disperse materials [3]. For research, chopped hygrothermically processed soy, carrots, and their functional mixtures were used. Vegetable tissues were ground to approximate size 4x2x3 mm. Conductive drying of samples by mass 0,3 g occurred in the working chamber of the calorimetric unit, at a temperature 60ºC, in conditions close to isothermal, until the equilibrium moisture samples are reached. Drying temperature 60°C was identified as optimal for pre-processed protein-containing feedstock, which prevents losses of biologically active substances. The mass of dry matter in the sample was determined by the method of drying inside the working chamber at 105 °C.

The actual values of the specific heat of evaporation of water from the sample were determined from the time of the establishment of the thermodynamic equilibrium inside the calorimetric chamber, using the formula:

$$r_i = \frac{\int_{\tau_{i-1}}^{\tau_{i+1}} q(\tau) d\tau}{m(\tau_{i-1}) - m(\tau_{i+1})}$$

where ri – specific heat consumption for evaporation in time from τi-1 до τi+1, kJ/kg;

τi-1 and τi+1 – the value of the current time point, sec;

q(τ) – the heat flux inside the working chamber as a function of time, J /sec;

m(τi-1) and m(τi+1) – sample mass in moments of time τi-1 and τi+1, kg.

The results of measurement are shown in Figure 1. From Figure 1, we see that at the beginning of drying, the heat of evaporation of moisture from carrots and soy-carrot mixture is approximately 4 ... 5% higher than the heat of evaporation of pure water. Mixing of components has led to the fact that in the process of drying, starting with a moisture content of 65%, in the mixture there is an exothermic reaction, which is accompanied by an additional heat release. It can be assumed that this is the reaction of the interaction of soy fat with carrot fat-soluble carotenoids, but more accurate determination of the nature of this reaction requires additional research.

Preliminary preparation of vegetative raw materials by the method of creating functional compositions with a specially selected ratio prevents oxidation of lipids and prolong the shelf life of processed soya and carrots.

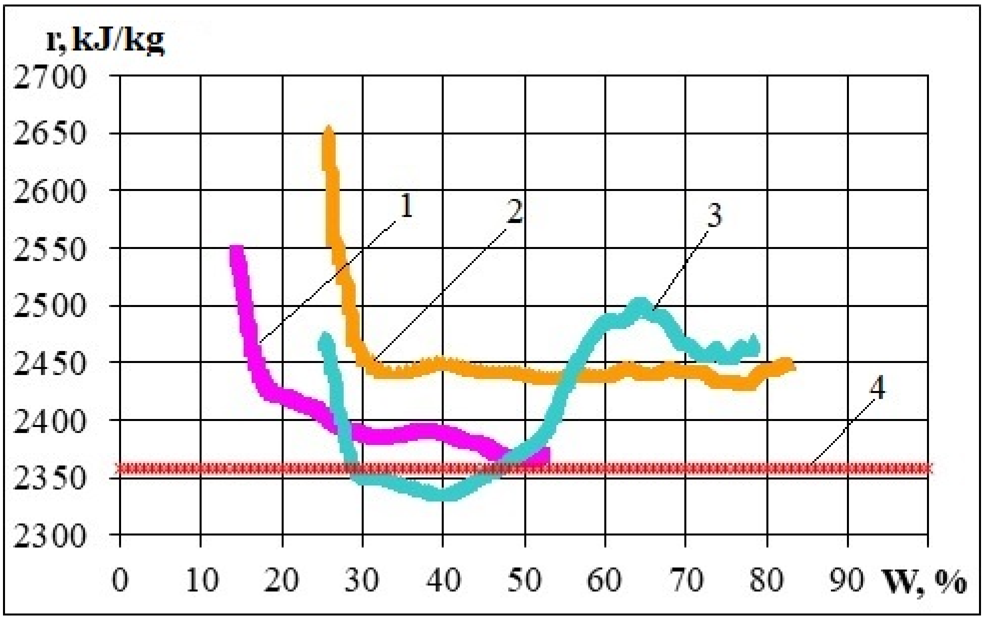

Fig.1. Dependence of the specific heat of evaporation of water from samples from there relative moisture during drying: 1 – soy, 2 – carrot, 2 - soy-carrot mixture, 4 – water.

Conclusion

It is established that specific heat expenses for evaporation of water from developed vegetable compositions based on soybean and carrot addition is smaller than it individual components. This can be explained by the fact that, when the composition of the proposed components is dried, a reaction occurs between the components of the mixture, which is accompanied by an exothermic effect. At humidity of a material from 50 - 30% specific expenses of heat of evaporation are lower than specific expenses of heat of evaporation of pure water. Due to the interaction of the components of the composition, the intensification of the drying process is taking place.

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Optimization of the composition of without clinker composite gypsum-lime binder

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Abstract – In order to optimize the content of metakaolin and amorphous silica in the composition of without clinker composite gypsum-lime binder the method of mathematical planning of the experiment was used. It was established that the maximum value of a compressive strength is achieved for the content of metakaolin 5.00% and amorphous silica – 3.75%.

Keywords – gypsum, quicklime, metakaolin, amorphous silica, compressive strength, normal density, curing, water resistance.

Recently, materials based on gypsum raw materials are widely used in construction due to low production energy costs. However, gypsum materials without modifying additives have low strength and water resistance [1]. One of the ways to increase the strength and water resistance of gypsum compositions is the introduction of quicklime and active mineral additives – metakaolin and amorphous silica.

To determine the optimal composition of the composite binder the mathematical planning with the use of two-factor experiment was carried. For changings of prescription levels of optimization (the amount of metakaolin and amorphous silica) the constant were the gypsum-quicklime ratio (1.5:1.0), the sum of all components (100%), the water-powder ratio (W/P = 0.80) and the temperature of the mixing water (T = 8–12 °C). As a chemical additive, a borax $Na_2B_4O_7\cdot 5H_2O$ was used in the amount of 0.5%.

It was defined by the analysis of the obtained mathematical dependencies that the use metakaolin in the amount of 3.5–6.5% and amorphous silica in the amount of 1.9–5.6% makes it possible to obtain a stone with a compressive strength 9.25–9.50 MPa (fig. 1).

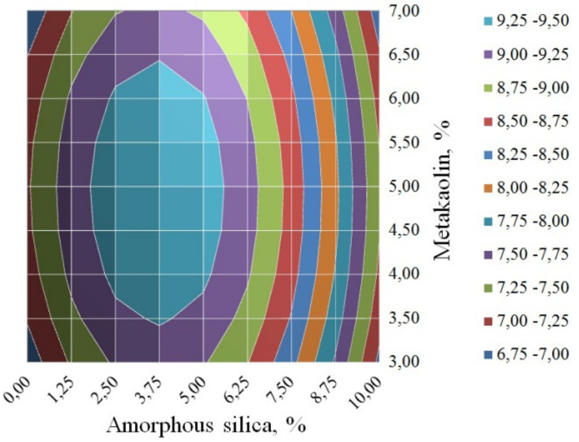

Fig.1. Isoparametric lines of influence of metakaolin and amorphous silica contents on the strength of gypsum-lime stone at the age of 28 days.

For optimized binder composition the normal density ND and curing time was defined: ND = 65%, curing beginning – not earlier than 10 minutes, curing ending – no later than 15 minutes. Stone based on an optimized gypsum-lime binder is characterized by increased compressive strength of up to 35% herewith water resistance is 0.57%.

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Foam layered apparatus with foam stabilization

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Abstract – In work were studied the expanded models of foaming apparatuses with gratings, made of tubes of different diameters. The questions of intensification of foam devices with the use of coarse-grating lattices are considered. The possibility of deep cleaning and practically complete cleaning of gases from ammonia and fluoride compounds with their separate absorption is noted.

Keywords – industrial gas emissions; cleaning process; hydrodynamics, mass transfer; foam apparatus; foam layer, research of purification processes; stabilization of foam layer; intensive apparatus

Introduction

In order to reduce energy consumption in systems for catching harmful and toxic substances, it is necessary to provide a reduction of hydraulic resistance while maintaining the high efficiency of gas streams cleaning. Given the controversial requirements for equipment and despite the large number of existing machines for mass transfer processes, the development of new highly intensive and efficient equipment is of considerable interest to environmental protection technologies in many industries.

Description of the problem

The most common method of purifying gas streams is methods for the absorption of harmful components from the released industrial gases. In this case, either the process of physical absorption occurs, or the absorbent enters a chemical interaction with the absorbed component (the process of chemisorption).

Recently, the direction associated with conducting diffuse processes in intensive regimes with developed turbulence at high speeds of gas and liquid flows has become relevant. Actually turbolization of the gas-liquid system leads to an increase in the intensity of mass-exchange devices. One of the methods of turbulization of gas-liquid systems is their transformation into mobile unstable foam due to the kinetic energy of gas.

Foam mode and foam devices of the "classical" type are described in and analyzed in a lot of works. Intensified apparatuses with foam layer stabilizer have been widely used for capturing dust from gases and for gas absorption in the chemical and related industries. Due to its high efficiency, high unit capacity, good operational qualities of their application, they can improve the stages of gas purification for technological and sanitary purposes, increase the efficiency of mass transfer and the reliability of gas-cleaning equipment. Industrial introducing the stabilization method of the gas-liquid layer significantly expands the scope of foaming devices and opens up new possibilities for intensifying technological processes with the simultaneous creation of low-waste technologies.

Based on researching the semi-industrial models of foam machines with lattices, assembled from tubes of different diameters, a pilot sample of foam absorber with the productivity of 12000 m^3/h of gas was designed [1].

One of the research directions was the absorption of ammonia by water in intensive foam modes with a stabilized foam layer. Absorption of ammonia by water is a typical process in absorber research to detect their effectiveness.

The process of absorption of ammonia in foam mode on counterproductive gratings of the usual type is quite fully studied at gas velocities up to 2,5 m/s. In order to compare the technological parameters of ammonia absorption in water under similar conditions, the work of the most common industrial counter processing grating with an area of free intersection of 0,18 m^2/m^2 and a diameter of holes of 5 mm was investigated.

The research of this grating was carried out both with the stabilizer, and without it. The research was due to the need to determine the degree of effect of the stabilization of the layer and comparison with the technological parameters of the newly developed design foam apparatus, as well as the establishment of the general nature of dependencies and kinetic parameters of the absorption process.

In order to verify the results obtained during bench tests in laboratory conditions, a cycle of pilot-industrial tests was conducted in which the main gas components were ammonia, fluoride compounds (mainly silicon tetra fluoride). In the system of purifying gases from the spray dryer, a reconstruction of the existing absorber was carried out (hollow scrubber with three tiers of nozzles). Instead of nozzles in the scrubber case, a contact step with coarse hole gratings (the holes are 0,045×0,045 m and $S_0 = 0,28\ m^2/m^2$) and a foam layer stabilizer were installed.

Conclusion

The conducted studies indicate the possibility of deep cleaning and virtually complete removal of harmful components from gases in their separate absorption. Dependences of NH_3 final content and fluorine in the gas after treatment from ammonium phosphate acidity shown that it is evident that the optimal mode for the absorption of these components lies within the pH of the solution from 3 to 5. In this case, the maximum permissible emission rates for ammonia are maintained. This is confirmed by the high mass exchange characteristics of the developed foam device, allowing the process of joint and effective cleaning of these components in the range of pH irrigating solution from 3 to 5 [2].

Acknowledgments

As a result of experimental and industrial tests, it is established the following: the efficiency of dust capture practically does not depend on the pH of the solution and also on the increase of the inlet dust to 4-6 g/m^3. Increasing the density of the circulating pulp of ammonium phosphates does not affect the efficiency.

The conducted studies have experimentally confirmed the possibility of effective mass exchange processes in an intensive foam layer on counter currently coarse hinged gratings.

The application of new apparatus allows radically reconstructing, with minimal cost, technological schemes for gas cleaning in the chemical and other industries to provide them with better operational and technological characteristics, while simultaneously increasing the efficiency of working with concentrated solutions, their circulation and use in the main process.

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UV curable cross-linked polymer and polymer-inorganic materials for fuel cell application

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***Abstract* – Proton conductive cross-linked membranes (polyacrylate copolymer and polyacrylate-silica nanocomposites) were synthesized by UV initiated polymerization in situ. Proton conductivity of membranes, investigated by impedance spectrometry, was found to be sufficiently high. Contact angle measurements allow to estimate free surface energy of synthesized membranes. The membranes also exhibit good thermal stability.**

Keywords – fuel cell, alternative energy source, proton conductive membrane, organic-inorganic material, acrylate, sol-gel precursor.

Introduction

A great progress in energy consumption during the last years causes increasing need in alternative energy sources [1]. One of the most promising energy sources are hydrogen and alcohols (mainly methanol), which are used as fuel in fuel cells. However, fuel cell technology needs to be improved significantly for practical realization and commercialization. In particular the creation of high effective proton exchange membranes is of a great interest as PEM determines the efficiency of the whole device.

The most commonly used are Nafion membranes which have excellent chemical stability and high proton conductivity. At the same time they suffer from methanol crossover and dehydratation at high temperaturers. So, new PEMs such as sulfonated aromatic membranes, graft membranes, blend membranes have been recently proposed and intensely investigated. Among different approaches UV curing seems to be suitable as this technique provides high reaction rate as well as the possibility to obtain thin films.

Results and discussion

Cross-linked copolymer membranes were prepared from the mixture of acrylic monomers, namely acrylonitrile (35 wt. %), acrylic acid (15 wt. %), 3-sulfopropyl acrylate potassium salt (25 wt. %) and cross-linker ethyleneglycol dimethacrylate (25 wt. %) by UV initiated polymerization (photoinitiator DMPA). Polymer-inorganic membranes were prepared from the same monomers and sol-gel system (SGS : TEOS – ethanol – water) using UV initiated polymerization *in situ.* The content of the added sol-gel system (wt. %) in membrane samples was as follows: S1 – 0; S2 – 1; S3 – 3; S4 - 5; S5 - 7.

Gel fractions of all the samples of the obtained membranes were high (>95 %). Membranes were converted to H^+ ionic form by immersion in HCl 0.1 M for 24 h.

Contact angle measurements using 2 liquids allow to estimate free surface energy and its components (dispersive and hydrogen ones) of the obtained membranes. The introducing of sol-gel system into the polymerizing formulations leads to hydrophobization of membrane surface and decreasing of the free surface energy. The results of the calculations using the known Owens-Wendt equation are summarized in Table 1.

Table 1

Values of contact angel measurement and free energy of membrane surface

N	Sample	θ, *degree* $C_3H_8O_3$	θ, *degree* CH_2I_2	λ_s^d, mN/m	λ_s^h, mN/m	λ_s, mN/m
1	S1	43,9	39,5	31,09	16,54	47,63
2	S2	39,8	37,1	31,56	18,21	49,77
3	S3	40,2	36,9	31,70	18,01	49,71
4	S4	42,6	35,2	32,16	17,16	49,24
5	S5	43,7	34,9	32,24	16,84	49,08

As one can see the sample S2 (containing 1 % added SGS) shows the increase of the hydrogen component of free surface energy, total free surface energy also increases. For the sample S5 (7 % of the added SGS) free surface energy is a bit less than for the sample S2, but it is larger than for the sample without the added SGS. So, silica component promotes water retention.

Proton conductivity of the synthesized membranes, measured by impedance spectrometry at 20ºC, is presented in Table 1. The values of proton conductivity are relatively high (10^{-4} - 10^{-2} Sm/cm).

Table 2

Sample	S1	S2	S3	S4	S5
σ, Sm/cm	$3.53 \cdot 10^{-4}$	$1.37 \cdot 10^{-2}$	$1.01 \cdot 10^{-3}$	$9.70 \cdot 10^{-4}$	$9.27 \cdot 10^{-4}$

Thermal behaviour of membranes was investigated by thermogravimetric method (Fig.1).

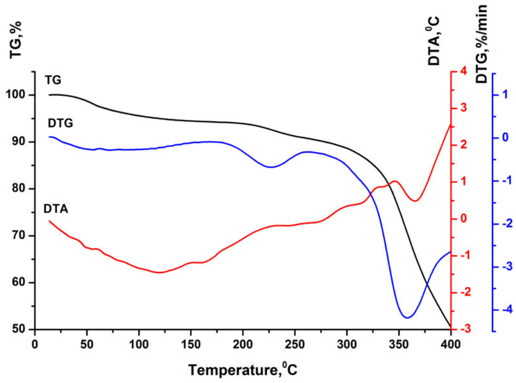

Fig.1. Thermogram for the sample S1.

The presence of the inorganic component in membrane leads to the increase in thermal stability – decomposition of sulfo groups in polyacrylic-silica membranes takes place at higher temperatures.

Conclusion

The synthesized polyacrylic and polyacrylic-silica membranes have high proton conductivity and thermal stability. The adding of TEOS-based sol-gel system promotes water retention and thermal stability. The materials are attractive as proton conductive membranes for fuel cell application.

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Synthesis of Styrene and Cyclopentadiene (Co)oligomers on the Basis of Fraction C9 of Oil Refining By-products

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Abstract* – *The production of styrenic and cyclopentadiene co-oligomers by oil refining by-products (hydrocarbon fraction C9) oligomerization studied. The combination of methods of low temperature suspension oligomerization and post-(co)oligomerization of unreacted hydrocarbons allow to obtain, on the basis of the hydrocarbon fraction C9, the styrenic and cyclopentadiene (co)oligomers, which differ in their properties and applications.

Keywords – liquid pyrolysis products, suspension (co)oligomerization, hydrocarbon fraction C9, cyclopentadiene, styrene.

Introduction

A significant amount (about 30%) of liquid by-products of pyrolysis (LBP) is formed at petroleum products pyrolysis (e.g. diesel fuel). Based on LBP hydrocarbon fraction C9 respectively, are obtained aromatic oligomers (so-called petroleum resins). They have a wide range of applications as film forming agents in lacquer-paint and anticorrosive coatings [1, 2].

The low-temperature suspension oligomerization can reduce the temperature and duration of the process compared to the existing technologies. Due to the low temperature of the process, the styrene monomers and their derivatives are introduced into the reaction. The resulting hydrocarbon resin is a styrenic (co)oligomer and is characterized by a low color index. Dicyclopentadiene (DCPD) is inactive in radical polymerization reactions. Cyclopentadiene (CPD) is polymerized by free radical mechanism. A cycle is revealed (monomerization) of the DCPD at temperatures 453-463 K with the formation of two reactive CPD monomers, by retro-dyenic reaction Diels-Alder synthesis [3, 4].

We proposed a two-stage method (Fig.1) for the synthesis of (co)oligomers of styrene and cyclopentadiene [5]:

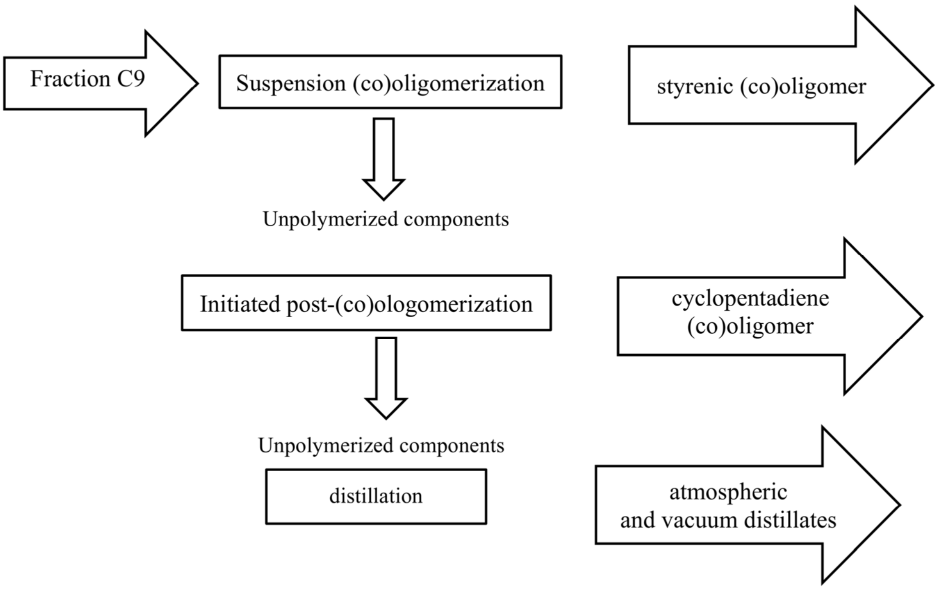

Fig.1. Two-stage method for the synthesis of co-oligomers of styrene and cyclopentadiene.

- the first stage – low-temperature (303-353 K) suspension or emulsion cooligomerization of fraction C9 hydrocarbons. At this stage, a styrenic (co)oligomer is obtained.
- the second stage is the thermal or initiated post-cooligomerization of unreacted hydrocarbons from the first stage. The temperature of the process is 453-473 K. At this stage, a cyclopentadiene (co)oligomer with a small number of parts of other unsaturated hydrocarbons of the C9 fraction is obtained.

Experimental Results and Discussion

Composition of the reaction mixture of suspension oligomerization:

- the dispersion medium - water;
- the disperse phase – liquid pirolisis by-products fraction C9 (density – 936 kg/m^3; bromine number – 68 g Br_2/100 g, molecular weight – 102, the content of unsaturated compounds to 45 %wt. especially: styrene - 17,85 % viniltoluene - 6,99 %, dicyclopentadiene - 18,00 %, indene 1,25 %.);
- the initiator is soluble in the disperse phase (1,0 %wt. calculated on the C9 fraction);
- suspension stabilizer – polyvinyl alcohol (0,1 %wt. calculated on the dispersion medium).

The suspension oligomerization of the C9 fraction was carried out in a three-necked flask equipped with a rotary stirrer. The resulting mixture was separated by centrifuge (4000 rpm).

Post-(co)oligomerization was carried out in thermostatically controlled sleeves at a temperature of 453 K for 6 hours, with the addition of a suitable initiator in an amount of 1.0% by weight. The choice of temperature is due to the composition of the fraction, namely the presence of a significant amount of dicyclopentadiene (about 13.6% by weight, calculated on the initial fraction) and its homologues. Unreacted hydrocarbons were isolated by atmospheric and vacuum distillation.

For the obtained (co)oligomers yield (calculated on the C_9 fraction), unsaturation (bromine number), color index by iodometric scale, softening temperature and average molecular weight were determined. The results are shown in Table. 1.

Suspension (co)oligomerization of unsaturated hydrocarbons of C9 fraction (first stage) ensures maximum yield of the product - up to 19.0% by weight (calculated on the C_9 fraction). Chromatographic analysis revealed that at first stage, the styrene monomers and its derivatives (vinyltoluene, methylstyrene) are introduced into the cooligomerization reaction. In the reaction mixture remaining after the separation of the (co)oligomer and distillation of the precipitant there are high-boiling reactive dicyclopentadiene, indene, residual styrene and its derivatives.

As a result of initiated high-temperature post-(co)coligomerization of unreacted residues (second stage) was obtained hydrocarbon resins with a high content of cyclopentadiene units. The cyclopentadiene (co)oligomer contains insignificant quantities of styrene and vinyl-toluene units that did not react at the first stage of the process.

The cyclopentadiene (co)oligomers obtained at the second stage is characterized by a lower index of unsaturation (22,2 - 27,8 g Br_2 / 100 g), a similiar softening temperature (350-358 K), a higher average molecular weight (640 - 700) and a significantly higher color index - 60 ... 80 mg I_2 / 100 ml (compared to styrenic (co)oligomers).

The composition of the (co)oligomers was determined basing on the data of the IR-spectroscopic analysis of the (co)oligomers samples of and the chromatographic analyzes of the C9 fraction and distillates.

Table 1

Yield, physical and chemical properties of (co)oligomers

Characteristics	Initiator		
	Benzoyl Peroxide	*tert*-Butyl Hydroperoxide	Cumyl Hydroperoxide
Suspension (co)oligomerization ([fraction C9] : [water] = 1:2; T = 353 K; τ = 3 hours; $C_{initiator}$ = 1,0 % wt.; $C_{stabilizer}$ = 0,1 % wt.)			
Styrene (co)oligomer yield, % by weight (calculated on the C9 fraction)	19,0	9,8	16,0
Bromine number, g Br_2/ 100 g	30,3	32,0	19.9
Softening point, K	354	340	350
Molecular weight (cryoscopy)	495	460	490
Color by iodometric scale, mg I_2/100 ml	20	30	30
Post-co-oligomerization ($C_{initiator}$ = 1,0 % wt., T = 453 K, τ = 6 hours)			
Cyclopentadiene (co)oligomer yield, % by weight (calculated on the C9 fraction)	19,8	30,1	25,7
Bromine number, g Br_2/ 100 g	20,4	22,8	23,4
Softening point, K	358	354	350
Molecular weight (cryoscopy)	700	640	670
Color by iodometric scale, mg I_2/100 ml	80	80	80
Total yield, % wt. (calculated on the C9 fraction)	*38,8*	*39,9*	*41,7*

Conclusion

The possibility of synthesis of styrenic and cyclopentadiene co-oligomers by two-stage method of oil refining by-products (hydrocarbon fraction C9) oligomerization was established. The two-stage method of the C9 fraction oligomerization allows to obtaine two types of oligomers with different physical and chemical characteristics. The total yield of oligomers is higher than with one-stage initiated high-temperature oligomerization.

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Operational, constructive and hydrodynamic parameters of foam devices

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Abstract – Industrial implementation of the stabilization method of the gas-liquid layer can significantly expand the field of foam applications and opens new opportunities for intensifying technological processes with the simultaneous creation of low-waste technologies. The basic parameters influencing the hydrodynamics of foam devices are determined, the basic constructions and operating modes of foam devices are considered. The connection of hydrodynamic parameters is revealed. The hydrodynamics of foam layer is considered.

Keywords – industrial gas emissions; cleaning process; hydrodynamics, mass transfer; foam layer, purification processes; stabilization of foam layer; intensive apparatus.

Introduction

The common method of purifying gas streams is the absorption methods for the absorption of harmful components from the released industrial gases. In this case, either the process of physical absorption occurs, or the absorbent enters a chemical interaction with the absorbable component (the process of chemical sorbtion). One of the promising directions of the intensification of the mass transfer process is the development of apparatus using the principle of interaction of gas-liquid flows in a layer of moving bodies, so-called foam devices with a three-phase fluidized bed of an irrigated nozzle.

Description of the problem

The problem of processing industrial gas streams is solved by conducting the process in an intensive mode. The industrial implementation of the absorption processes in the foam layer and the use of the stabilization method of the gas-liquid layer greatly extends the scope of foaming devices and opens up new opportunities for the intensification of technological processes with the simultaneous creation of low-waste technologies. And the use of modern designs of suspended nozzles allows to upgrade existing absorption units.

Usually empty bulbs with a diameter of 20 - 50 mm and a density of 100 - 900 kg/m^3, made of polyethylene, polypropylene, rubber and other relatively light materials, as a rule, were used as nozzle bodies in an absorber with a three-phase fluidized bed. On previously examined nozzles, fluidized bed apparatuses were used mainly in technological cycles with significant specific loads on gas and liquid, which led to high energy consumption. At the same time, in systems for cleaning industrial gases from harmful components present, as a rule, in low concentrations, it is necessary to ensure a high degree of gas purification with minimal liquid flow.

A new volumetric hollow nozzle was developed. The advantage of this nozzle is the transition to a fluidized state at relatively low gas velocities, as well as a developed contact surface of the phases. The funnel structure from which the nozzle is made allows to achieve higher values of the mass transfer coefficients due to the effect of the formation of the film in cells of small size. The nozzle has high porosity and low hydraulic supports. Depending on the material selection, the nozzle can have different wettability.

New nozzles are simple in design and have a relatively low cost, which allows them to be effectively applied in the processes of purifying the gases leaving in different industries, in cooling towers of circulating water supply systems, in a number of other processes of heat and mass transfer.

Apparatus with a weighted nozzle differs from other by chaotic and pulsating character of movement of the elements of the nozzle in a weighted state. Apparatus with a weighted nozzle can be sectioned, that is, they use different partitions, inserts, stabilizers or grids of a large free section, which divide the section of the apparatus and its working area into separate sections. Such devices successfully solve the problem of large-scale transition from laboratory models to industrial columns without a special change in the efficiency of mass and heat transfer.

The most widespread in the industry are devices with a weighted (fluidized) nozzle, which are constructively simpler and can be improved in the direction of reducing energy consumption, which is important for gas cleaning processes.

Visual observations during the process show the existence of several hydrodynamic modes of operation of devices with a moving nozzle. These regimes are called - initial intermediate, developed (complete) fluidization, stenosis of the apparatus; or - the beginning of fountain (weighing), transition mode, mode of developed turbulence and mode of flooding. In devices of small diameter with a constant value of the mass velocity of a liquid, depending on the speed of gas, four hydrodynamic modes can be distinguished. In the mode of initial pseudosuppression there is a "fountain": they pass into the fluidized state of the nozzle bodies only in the central part of the apparatus, remaining stationary under the walls. The liquid flows down the surface in the form of a film. In the mode of intermediate fluidization, the body bodies located near the walls begin to move down and pass into the central part of the apparatus. In the mode of developed (full) fluidization, all nozzle bodies are in a fluidized state, circulating inside the apparatus: in the central part the movement is directed upwards, and under the walls - downward. The amount of liquid contained in the apparatus increases and it is present mainly in the form of droplets or in the composition of the gas-liquid structure, which is close to the bubble layer.

Together with the subsequent increase in gas velocity, the amount of fluid retained in the layer increases, which, in the end, leads to the flooding of the apparatus.

In addition, on the hydraulic resistance of the device with a three-phase layer, the resistance of the support-distributing plate is significantly affected by the hydraulic resistance of the apparatus: the less the free cross section of the plate, the greater the deviation in the graph of the dependence of the hydraulic resistance on the speed of gas in the apparatus from the horizontal line in the mode of developed fluidization.

Conclusion

An analysis of a number of studies [1-2] shows that the promising direction of the intensification of the mass transfer process is the development of apparatuses with a three-phase fluidized bed of irrigated nozzle of complex forms with mesh materials. For gas cleaning systems from gaseous components, it is necessary to provide small loads on the liquid while maintaining a high degree of purification. This can be achieved by using a drip tray with a small free section and a newly designed nozzle.

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Technological aspects of obtaining dried pectin-containing products

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Abstract* – *The results of research hygrothermal processing and the process convective drying of pectin containing raw materials are presented. These processes contribute to the intensification of drying, the reduction heat consumption and provide a high degree of conservation pectin substances.

Keywords – pectin-containing raw material, hygrothermal processing, intensificatin of drying

Introduction

In most countries of the world production of pectin as an integral component of many food products is characterized by a constant tendency to increase. There is no industrial production of pectin in Ukraine. So the pectin requirements are satisfied by import, and the range of pectin-containing products is limited. Under such circumstances it is worthwhile to use pectins entering into the composition of the raw materials themselves, in particular, the dried fruit-vegetable products. In addition, the latter are of high nutritious and biological value of themselves and can serve as an alternative version of food form of pectin.

Results of investigations

Apples, beets, pumpkins, quinces, currants, etc., are the source of vegetable pectin-containing materials. The content of pectin substances is from 1,0 to 2,0 % for raw mass depending on crop type, sort indicators, climatic conditions and aging degree. This specifies their application as processing objects when producing dried pectin-containing products (such as dried fruits, chips, food powders, etc.).

An increased content of pectin substances with the inherent ability to bind and retain moisture complicates process and limits material temperature and duration of thermal dehydration. Taking into account energy intensity of dehydration as well as increased requirements to quality and safety of the end products, the maximum permissible temperature of dehydrated material as well as naturalness of dry products and ecological purity of the technological process are at the foreground.

The results of both theoretical and experimental investigations demonstrate that hygrothermal processing of parenchymal tissues is a sine qua non for processing pectin-containing raw material. Such operation is doubly grounded. Firstly, it promotes hydrolysis of insoluble pectin (protopectin) to its soluble form; as a result, the jelly-like properties of dried products increase. Secondly, along with the specific influence on changing the initial raw material properties, the material color becomes stable, the ferment system is inactivated and the cell permeability increases. Further, during convective drying, the moisture exchange is intensified by 10...15 %.

When grounding the production technology for pectin-containing dried products, we proved that avoidance of material temperature excess over the permissible value and reduction of heat loss are ensured by a number of methods, in particular, by drying at high-moisture high-temperature dehydration [1]. An example of such dehydration is presented in fig. 1 (curves 2 and 2'). In accordance with the process parameters, the drying agent temperature t = 120 °C and moisture content of dry air d = 100 g/kg are sustained for 40 min; then the temperature is reduced to 80 °C and moisture content of dry air is reduced to 10 g/kg.

A comparative analysis of moisture exchange kinetics using the curves $W^c = f(\tau)$ and drying rate $dW^c/d\tau = f(W^c)$ shows presence of a period of constant rate at all studied modes (curves 1',2' and 3'). It comes to an end when the material reaches the first critical moisture content W^c_{cr1} in the range from 260 to 350 % depending on the hydrothermal modes. The longest period of constant rate is observed at the high-moisture high-temperature mode. In this case the material temperature is equal to that of a "wet" thermometer which is much higher as compared with the case of the 1,1' and 3,3' modes. At higher temperature moisture diffusion from the inner layers of dehydrating material to the surface is considerably higher; so the intensity of such mode is the highest. Duration of the period of constant rate is 30 % of the total time; the process is reduced by 20 % as compared with drying in the 80 °C mode (curve 3). In such case, the favorable conditions arise for protopectin hydrolysis into a soluble form. The two stages of technological processing (hygrothermal treatment and thermal dehydration) are combined into a single process. It is determined that the soluble pectin amount in fresh apples is 35 % of the total pectin amount and increases to 58 % after hygrothermal processing. Some insignificant loss 2...4 % of the total amount of pectin substances and grows of soluble pectin amount by 2...5 % in the course of drying process are observed. This is supported by the diagram in fig. 2.

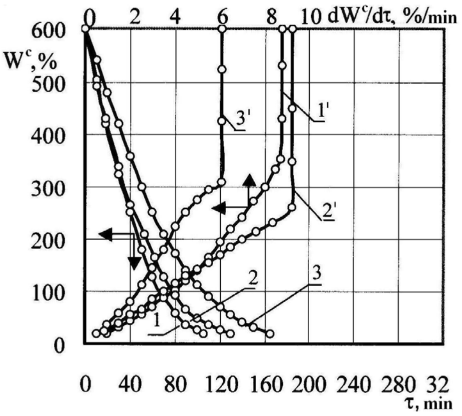

Fig. 1. The effect of moisture content and heat carrier temperature on the apple drying process $g = 36$ kg/m^2; $V = 1$ m/s; $d = 10$ g/kg of dry air: 1,1' – $t = 120$ °C; 3,3' – $t = 80$ °C; 2,2'–$d = 100...10$ g/kg of dry air; $t = 120...80$ °C.

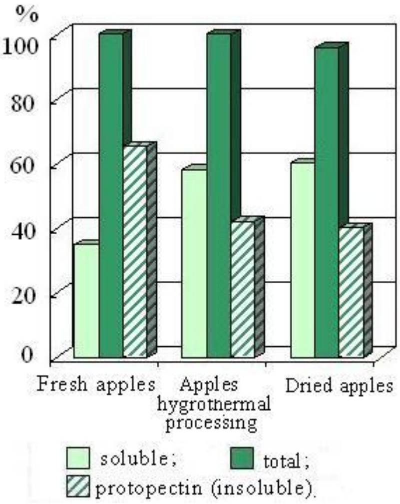

Fig. 2. Changes of pectin form ratios in the course of processing.

Conclusion

According to the results of investigations, the stepped modes of dehydrating pectin-containing materials are determined. They promote a reduction of process duration by 20 % and saving in the energy resources by 15 % as well as guarantee a high level of conservation of pectin and biologically active substances.

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Theoretical analysis of the energy efficiency of the filtration drying at the high pressure

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Abstract – The estimates of energy consumption were performed for two methods of drying: filtration drying at the normal pressure and filtration drying at the high pressure. It is shown that the energy consumption for filtration drying at the normal pressure is higher than in the same drying mode at high pressure.

Keywords – drying, filtration drying, energy consumption, high pressure, compressor.

Introduction

In modern conditions, the problem of energy saving in production and economic activity is especially urgent because of the fast rise in prices of energy resources. One of the most energy expensive processes of the food industry is the process of drying. According to T.Kudra [1] the drying process takes 25% of national energy consumption in industrialized countries, and in the food and processing industry it takes to 30%. In the context of high cost of energy even 1% of savings in energy consumption brings significant economic results. The average coefficient of efficiency of convective dryers is 12-80% with most of the losses is accounted for the exhaust drying agent (40%). In this connection the issues of energy savings are solved in two main ways: the development of new methods of drying and the development of new technological methods of the dehydration process.

Materials and methods.

The aim of study is ground of the possibility of increasing of energy efficiency of the drying process under the influence of the of high pressure in filtration drying.. According to proposed method of drying [2], wet crushed material is placed in a sealed eveporation module (EM) where overpressure created by an external compressor. In the result of compression of air in the compressor is heated to the required temperature. When air filtering through wet porous material is fully saturated to the state of condensation of steam and then under excess pressure derives from EM. Dried zone is gradually moving from input to output EM. This drying agent completely using its drying capacity, cooled closely to ambient temperature as a result of displacement of steam fluid mixture from porous structure. As a result is absent losses of heat from the drying agent, because, as indicated above, this is the main reason for the low efficiency of convective dryers. In this method the drying heater and fan functions combined in one device - compressor, eliminating additional energy to move the drying agent as in convective dryer.

Results and Discussion

We shall considered two dryers – filtration drying at the normal pressure and filtration drying at the high pressure, which is working at the same mode when drying agent completely saturated with moisture to relative humidity φ_2=1 at the output of the dryer. Although, for convective drying of such mode in practice is not used (usually φ_2=0,5 - 0,6), but humidity φ_2=1 at the output of the dryer is the theoretical limit of efficiency of convective drying (at normal atmospheric pressure). For filtration drying at high pressure, as indicated above, this mode is the basic operating mode. Productivity on evaporated moisture for both dryers taken the same as the temperature of the drying agent.

As you know, the temperature of the adiabatic compression process in the compressor is connected to the pressure thus

$$t_1 = (t_0 + 273)\left(\frac{p_1}{p_0}\right)^{\frac{\gamma-1}{\gamma}} - 273\,, \tag{1}$$

where t_0, t_1 - temperature at the inlet and outlet of the compressor °C;

p_0, p_1 - pressure at the inlet and outlet of the compressor, Pa;

γ - adiabatic index of air ($\gamma = 1{,}4$).

Calculation of this formula shows that with increasing pressure from 0.15 MPa to 4 MPa temperature at the outlet of the compressor increases from 60°C to 160°C (actually in compressor the process is polytropic and $\gamma<1.4$ respectively outlet temperature slightly less).

The calculations assumed that for convective drying heater should heat the air to a temperature t_1 at normal atmospheric pressure. In filtration drying temperature is provided by compression in the compressor to the appropriate pressure p_1. To calculate the parameters of humid air we used classical equation [3]. The air parametrs at the outlet of the dryer was determined for isenthalpic drying process.

We obtained formulas total specific energy consumption for the filtration drying process at normal pressure and high pressure.

Total specific energy consumption for the filtration drying process at normal pressure is equal to the sum of thermal and hydrodynamic losses

$$E_1 = \frac{\upsilon_{a0}}{d_2 - d_0}\left[\rho_{a0} C_{a0} (t_1 - t_0) + (p_1 - p_0)\right]. \tag{2}$$

where E_1 - specific energy consumption of filtration drying at the normal pressure and filtration drying at the high pressure, J\/kg.

In the case of filtration drying under high pressure all the energy brought to the compressor is spent both on heating the drying agent and on overcoming the hydrodynamic resistance of the material layer. In addition, in the case of pressure drop between the EM and the surrounding environment positive work may carried out when the gas is expanded in the throttle from the pressure p_2 to the pressure p_0. This additional work is carried out only when there is a drop in pressure on the throttle, that is, only in the case of filtration drying under the action of high pressure.

$$E_2 = \frac{p_0}{(d_2 - d_0)(\gamma - 1)}\left\{\upsilon_{a0}\cdot\gamma\left[\left(\frac{p_1}{p_0}\right)^{\frac{\gamma-1}{\gamma}} - 1\right] - \upsilon_{a2}\left(\frac{p_2}{p_0}\right)^{\frac{1}{\gamma}}\left[1 - \left(\frac{p_0}{p_2}\right)^{\frac{\gamma-1}{\gamma}}\right]\right\}, \tag{3}$$

where E_2 - specific energy consumption of filtration drying at the normal pressure and filtration drying at the high pressure, J\/kg;

d_0, d_2 - moisture content of the air at the inlet and outlet of eveporation module, (kg steam)/(kg dry air);

ρ_{a0} - air density, kg/м^3;

υ_{a0}, υ_{a2} - specific volume of air at the inlet and outlet of eveporation module, м^3/kg;

C_{a0} - specific heat of air, J/(kg·K);

p_1, p_2 - pressure at the inlet and outlet of eveporation module, Pa;

The calculations were carried out in Mathcad. Standard data of the pressure of saturated steam were used [4]. In calculations of specific energy consumption, constant parameters of the ambient air were used: t_0=20 °C; d_0= 0,01 kg/kg, p_0=101 kPa. The parameters of the drying agent at the outlet of the dryer were calculated in the conditions of the isoenthalipic drying process (absence of heat losses inside the dryer) under the conditions of the given relative humidity at the outlet of the dryer (φ_2 = 0.6 - 1.0) and given pressure p_2.

The simulation results are listed below. In Fig. 1 a comparison of specific energy consumption in two processes of filtration drying are shown for a typical temperature range of the drying agent 40 - 160 ° C, which corresponds to compression pressures in a compressor of 0.11 - 0.4 MPa. In calculations, the hydrodynamic resistance of the layer was assumed to 5 kPa, which corresponds to the usual thickness of the layer 50 - 100 mm for filtration drying at normal pressure.

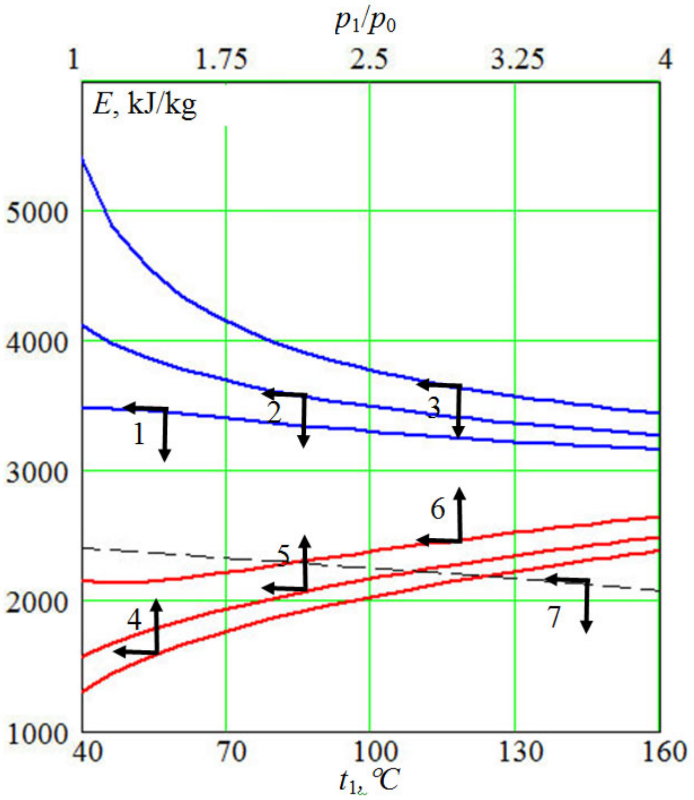

Fig.1. Specific energy consumption for two methods of filtration drying with constant hydrodynamic resistance Δp= 5 kPa and different outlet air humidity: filtration drying at the normal pressure: 1 - φ_2=1; 2 - φ_2=0,8; 3 - φ_2=0,6; filtration drying at the high pressure: 4 - φ_2=1; 5 - φ_2=0,8; 6 - φ_2=0,6; 7 - specific heat of water vaporization.

From the above graphs, it follows that the specific energy consumption for filtration drying at normal pressure decreases with increasing temperature and for filtration drying at high pressure increases with increasing pressure (temperature). This is due to the fact that with increasing temperature of the drying agent, its absorption capacity (d_2 - d_0) is greater under normal atmospheric pressure than in the case of high pressure. Reducing the degree of saturation of the drying agent at the outlet of the dryer increases the energy consumption proportionally. It is which is quite understandable, since the specific energy consumption is inversely proportional to the difference in moisture content at the outlet and inlet of the dryer (d_2 - d_0).

For a constant hydrodynamic resistance of a filtration layer at 5 kPa, the specific energy consumption for filtration drying at normal pressure is 3200 - 5400 kJ/kg (curves 1 - 3), whereas for filtration drying at the high pressure 1400 - 2700 kJ/kg (curves 4 - 6), that is, in a certain range of temperatures (pressures) even less than the specific heat of water vaporization. This is explained by the well-known fact that the energy conversion factor in heat pumps, where the useful work of the cycle is equal to the difference between work of the compression and expansion of the gas, is also greater than one unit. In the case of filtration drying under high pressure, this is explained by the fact that the expansion of the drying agent is spent on removing free water in a liquid state. The amount of that free water is difficult to determine, but it is well known from the experience of filtration drying that it is removed and even more so the greater the pressure difference applied to the product layer.

As calculations shows, with the increase of the hydrodynamic resistance of the layer, the energy consumption of the drying process increases for both method of drying under normal pressure and drying at a high pressure. But increasing the pressure allows you to dry a larger layer of material compared to filtration drying at normal pressure. Accordingly, this allows a proportional increase the length of the drying chamber and significantly simplifies the design of the dryer of continuous action, using a cylindrical section of the chamber with a large length to diameter ratio.

As shown by the modeling of the dependence of specific energy consumption on the compression ratio for filtration drying at high pressure there is a minimum energy consumption for a certain hydrodynamic resistance and drying temperature. This is explained by the fact that on the one hand, with the increase in the pressure of injection at a constant hydrodynamic resistance, the expansion of the gas at the outlet of the dryer increases, which is spent on squeezing the moister, on the other hand, with the increase of the pressure of injection, the absorption capacity of the drying agent decreases in comparison with the normal pressure.

Conclusion

A theoretical comparison of energy efficiency of the filtration drying process under the influence of high pressure and filtration drying at normal pressure is carried out.

It is shown for filtration drying at high pressure, the specific energy consumption is 1.5 - 2 times less than in the filtration drying at normal pressure, and under certain conditions may be lower than the latent heat of evaporation of water.

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Obtaining and properties of active charcoal from pyrolized wood waste

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***Abstract* – Activated carbon (AB) with a high yield, developed specific surface (mainly with micropores) was obtained by the method of alkaline activation of pyrolyzed wood waste from the smoking industry (carbonized chips (CC). Their high sorption capacity toward phenol, lead ions and dye - methylene blue (MB)wass determined.**

Keywords – waste of smoke production, alkaline activation, surface, sorption, pollutants

Introduction

The search for economically feasible ways to obtain cheap sorption materials to clean contaminated environments remains an urgent problem for the whole world. Among such materials, a significant place is occupied by carbon sorbents, the raw material for which there is a wide range of precursors (natural coal, peat, wood, carbon waste of different genesis). But only 2% of various types of waste are used for the production of sorbents, although the reserves are very large. For solving special problems of alcoholic beverage production (LBP) it is important to obtain activated carcoal (AC) with certain properties from available renewable raw materials.

The real prospective raw material for the manufacture of such sorption materials may be wood waste from the smoke industry. They are formed during the pyrolysis of woody chips as hard-core rocks (beech, alder, oak, elm, linden, maple, etc.), and wood pecker chips (cherry, cherry, apple, apricot, plum). The purpose of our work was to evaluate the properties of potential sorbents, obtained from technological waste of the food industry. They must be suitable for cleaning various environments, including water-alcohol raw materials.

Experimental

The wood waste obtained with smoking of food products (humidity W_1 = 67-82% was dried in air (T_1 = 293-298 K) during $\tau_1=(336\text{-}504)\cdot 60^2$ sec, then dried at a temperature T_2 = 373-383 K to an air-dry state with humidity W_2 = 4-8%. As an activating agent, potassium hydroxide (KOH) was used which was injected by CC impregnation with an aqueous solution of KOH and maintained for $\tau_9=(18\text{-}24)\cdot 60^2$ sec at T_8 = 291-295 K, then dried at T_9 = 373-383 K to moisture content W_{10} = 4-8%. Then the blend was activated in an argon current with volumetric flow rates - $Q \leq 5.6 \cdot 10\text{-}7$ m^3/s at non-isothermal heating of 0.07 deg/s to T_{10} = 873-1073 K [1].

The conditions for obtaining AC from CC and some product characteristics are given in the table in comparison with those for charcoal sorbents, obtained from lignite. It can be seen that the sorbents from the carbonized wood waste have better some indexes, then tested samples. These are the consumption of the activating agent, the product yield and sorption activity toward some pollutants. The comparison of the distribution of pores in the sorbent from lignite and in the AC from the waste smoke production is shown in the figure. The CC sorbent is predominantly microporous, which makes it promising for use in a wide range of processes.

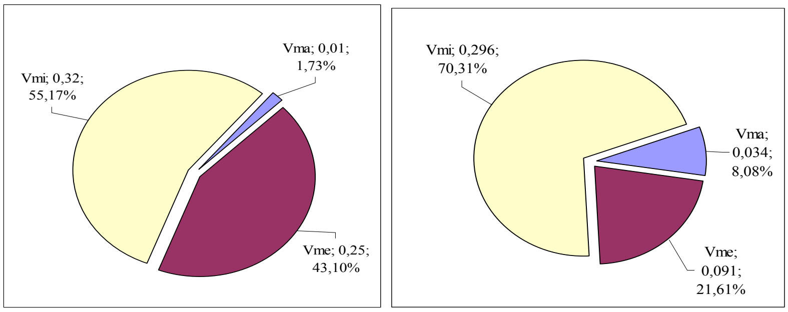
The best result on the quality of the vodka according to the results of the findings of 3 professional tasters was set for AB from waste of smoke production, activated alkaline. Estimates of the vodka purified by it were 9,68-9,70 against 9,4-9,6 for the initial sorting and after purification with the sorbent, obtained from CC, activated by orthophosphoric acid [2].

Table 1.

Conditions of obtaining an AC and its characteristics

Index	Units of measurement	Title of index	AC from lignite		AB from CC	
Activation temperature , K			1073		1073	
State of activating agent KOH			solid		50%-solution	
Raw material / agent, kg / kg			1:0,5		1:1	
Y	%	Yield	39,0		70,4	
S_{BET}	m^2 / g	Specific surface	890		777	
V_{Σ}	cm^3 / g	Total volume of pores	0,58	100 %	0,42	100%
V_{ma}	cm^3 / g	volume of macropores	0,01	1,7 %	0,03	8,1 %
V_{me}	cm^3 / g	volume of methopores	0,25	43,1 %	0,09	21,6 %
V_{mi}	cm^3 / g	volume of micropores	0,32	55,2 %	0,30	70,3 %
V_{1nm}	cm^3 / g	volume of subnanopores	0,23	39,7 %	0,25	59,2 %
A_{Φ}	mg / g	Sorption of phenol	120		200	
A_{Pb}	mmol / g	Sorption of Pb^{2+}	–		0,7	
$A_{\text{МБ}}$	mg / g	Sorption of MB	92		150	

Positive moments of our research process were energy saving, high yield and sufficient mechanical strength (MP ≥80%) of the product. It is also important that during the conversion of the pyrolyzed chips into the adsorbents, tars are no eliminated (thus, the load on the environment is much less than when activating, for example, peat or coal).



A B

Fig.1. Distribution of pores in AC: a - from lignite; B - from the waste smoke production (CC).

Conclusion

The proposed approach allows to obtain the solid carbon sorbents from wood waste from the smoke industry by the method of alkaline activation. The process will result in a high yield (70-80%) of the product with a developed specific surface and pore space, a high sorption capacity to some pollutants, and also a fractional composition of the particle size that is adapted to the technology of distillery production.

Acknowledgments

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Secondary plant material is the rational alternative in veterinary medicine

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Abstract – Nowadays, antimicrobial resistance is a growing problem. The issue is the development of medicinal feeds containing active active substances of biological origin instead of antibiotics. Therefore, we have been conducting research on extracts of thyme waste. It was established that the thyme extract contains sufficient flavonoids and exhibits antimicrobial activity.

Keywords – antimicrobial resistance, thyme, waste, flavonoids, antimicrobial activity.

Introduction

Antimicrobial resistance to medicinal products for human use and veterinary medicinal products is a growing health problem in the Union and worldwide. Due to the complexity of the problem, its cross-border dimension and the high economic burden, its impact goes beyond its severe consequences for human and animal health and has become a global public health concern that affects the whole of society and requires urgent.

Environmental incidents that are observed following the administration of a veterinary medicinal product to an animal should also be reported as suspected adverse events. Such incidents may consist, for example, in a significant increase of soil contamination by a substance to levels considered harmful for the environment or in high concentrations of veterinary medicinal products in drinking water produced from surface water [1].

Consequently, the issue is the development of medicinal feeds containing active active substances of biological origin. Oregano, thyme, garlic, horseradish, chili pepper, peppermint, cinnamon, anise are used as natural growth stimulants for farm animals [2].

The technology of feed manufactoring involves the addition of antioxidants, preservatives, biostimulants and components intended for the treatment and prevention of animal diseases in their composition. Nowadays, investigations on secondary metabolites recovery from plant and by-products are increasing due to consumer's awareness of its health and nutraceutical benefits. Currently, many studies have focused on agricultural and industrial wastes in the search for natural antioxidants. One of the approaches is to use as raw material components of the feedstock of plant raw materials [3, 4].

Results and Discussion

In order to solve this problem, the content of the biologically active substances and the antimicrobial activity of Thymus vulgaris waste after the production of the medicinal product Pertusyn syrup was studied.

Plant compounds especially phenolic compounds such as flavonoids, phenolic acids, tannins are very important components for the free radical scavenging and antioxidant activities of plants. This family of compounds acts as antioxidants and thereby protect from degenerative diseases in which reactive oxygen species (ROS) are involved. Therefore, the aims of the present study were to evaluate the efficiency of the secondary extraction to receipt polyphenolic compounds and to determine it biological activity.

Quantitative detection of the TFC was carried out using Cary-50 Varian spectrometer the method of definition is described in [5].Total flavonoid content is 0,92 % expressed of rutin.

To evaluate the antimicrobial activity following bacterial species were used: Gram-positive Staphylococcus aureus ATCC 6538-P, Bacillus subtilis ATCC 6633 and isolated from soil:

Staphylococcus hyicus, Micrococcus luteus; gram-negative: Pseudomonas aeruginosa ATCC 9027, Escherichia coli ATCC 8739, Salmonella Abony CIP- 8039 and isolated from the environment Acinetobacter johnsonii, Moellerella wisconsensis; the fungi: Candida albicans ATCC 10231, Candida utilis Lia-01, Saccharomyces cerevisia ATCC 9763, Aspergillus brasiliensis ATCC 16404. Determination of antimicrobial activity using the diffusion into agar. The results of antimicrobial activity studies is that 70% aqueous-alcoholic extract appear to be more effective than 40% extract, namely: the growth inhibition zone diameters reached 14,00-24,00 mm towards both Gram-negative and Gram-positive bacteria. In This means that both extracts have a good antibacterial activity. Regarding yeasts and mold, the diameter of the growth inhibition zone reached 11,00-14,00 mm, which also indicates moderate fungicidal activity of the extracts.

Conclusion

Our studies indicate that waste of hop cones with 96% ethanol contain quite high amounts of interesting biologically active compound, including flavonoids.

The effectiveness of the proposed solution is to contribute to the program to combat antibiotic resistance, rational use of the resources of the planet and increase the profitability of production. Another important factor in the effective use of biologically active compounds of thyme in feed additives is their effect on technological parameters, namely, productivity, feed conversion, carrier, carrier peak, and others. Natural secondary plant ingredients are an effective alternative.

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Ratio between Heat and Mass Transfer when Concentrating the Solution in a Cooling Tower

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Abstract* – *The ratio between the intensity of the mass transfer in gas and the heat transfer in liquid during the evaporative solution concentration has been studied. It was determined that the share of liquid resistance in the total resistance to enthalpy transfer increases in the temperature range from 30 to 50 °C by almost 2 times, and reaches 40 %. The technique has been developed for the separate determination of the mass transfer coefficients in gas and heat transfer in liquid.

Keywords – concentrating solution, cooling tower, mass transfer, heat transfer, resistance to enthalpy transfer, step phase contact, fall-through trays.

Introduction

Cooling towers, originally designed for concentrating solutions containing sodium chloride, are now used almost exclusively for evaporative water cooling in industrial water circulation systems. The negative effects of such systems on the environment are due to the need for temporary or continuous replacement of high salinity water for fresh. This disadvantage can be turned into advantage by returning to the original purpose of the cooling towers and using technological solutions that need to be concentrated for apparatuses cooling.

Evaporative liquid cooling during its direct contact with air is due to the complex combination of heat and mass exchange. This study is devoted to identifying the ratio between the rates of these processes and identifying the stages that determine the kinetics of solution concentration. For evaporative cooling and solution concentration, a cooling tower [1] with a step phase contact, equipped with fall-through trays with large free cross section and large (50-100 mm) holes, is to be concerned. The research was conducted in relation to the mentioned apparatus design.

Literature Review

In the theory of evaporative cooling [2], "dry" and "wet" heat exchange are distinguished. The former is due to the temperature difference of the contacting phases, the latter is due to the thermal effect of water evaporation or condensation. Both of them are closely related, which complicates the calculation for the cooling tower using the traditional equations of heat and mass exchange. To simplify the calculations, it was proposed (see, for example, [3]) to consider heat transfer due to both mechanisms, as a whole process, the driving force of which is the difference between the actual specific air enthalpy in contact with the cooling liquid, and air in equilibrium with this liquid. In this case, the kinetics of heat transfer between the contacting phases is described by the following equation:

$$G\,\frac{\mathrm{d}H_g}{\mathrm{d}S} = k_H\,(H_g - H^*), \qquad (1)$$

where G is the mass air flow, kg/s; H_g and H^* are the air enthalpy in contact with the cooling liquid and the air in equilibrium with this liquid, respectively, kJ/kg of dry air; S is phase contact surface, m^2; k_H is enthalpy transfer coefficient, kg/m^{2}s.

The enthalpy coefficient k_H is determined with the following formula:

$$\frac{1}{k_H} = \frac{1}{k_g} + \frac{H^* - H_i}{\alpha_l (t_i - t_l)}, \qquad (2)$$

where k_g is the mass transfer coefficient in gas, kg/m^{2}s; α_l is heat transfer coefficient of the liquid, W/m^2·degrees; t_i, t_l are surface temperatures of the gas and liquid interface and the main mass of the liquid, respectively, °C, H_i is the air enthalpy in equilibrium with the solution at temperature t_i.

According to equation (2), the total resistance to enthalpy transfer is the sum of two terms, the former determining the resistance in the gas, and the latte determining the resistance in the liquid phase. The studies of nozzles for traditional cooling towers [4] show that resistance of liquid is from 27 to 46% of the total resistance to enthalpy transfer. Data on similar studies performed for fall-through trays are missing.

Research methodology

The experimental study of the evaporative solution concentration using the fall-through trays was carried out at a set that included an experimental apparatus, a set of auxiliary equipment and a set of measuring instruments. The experimental apparatus consisted of a base with built-in pipelines for air supply and drainage of the solution, three shells installed on it with a diameter and height of 0.5 m, and a lid equipped with a pipeline for air outlet and a device for distributing the solution entering the apparatus. The trays to be examined were mounted between the side-bars, i.e. disks punched with 25 holes 65 mm in diameter evenly distributed over the square. The free section of the trays was 42%. The salt solution (brine) with a mass fraction of NaCl 24–25% was subjected to concentration in the set.

Research results

In order to make sure that there is a significant resistance to enthalpy transfer of the liquid, a series of experiments was performed in which the temperature of the initial brine varied within 35-70 °C. The results are presented in Fig. 1 as the dependence of the enthalpy transfer coefficient on the average temperature of the liquid in the apparatus.

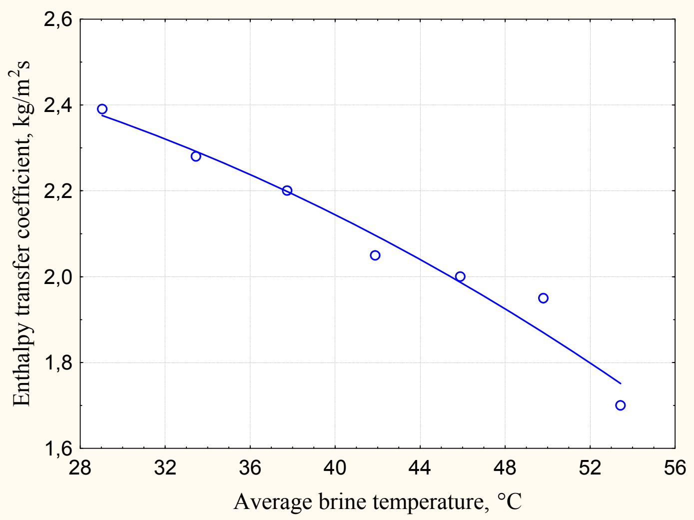

Fig. 1. Dependence of enthalpy transfer coefficients on temperature.

As it can be seen from the graph, when the temperature increases from 29 to 53 °C, the value of k_H falls by more than a third and with an increase in temperature, the tendency for k_H falling increases. Such a strong influence of temperature on the enthalpy transfer coefficient can be explained by analyzing equation (2).

As it is well known, temperature has little effect on the mass transfer coefficients in gas, k_g, and heat transfer in liquid α [3]. At the same time, the factor of the term $\left(H^* - H_\mathrm{i}\right)\big/(t_\mathrm{i} - t_\mathrm{l})$, which determines the resistance to enthalpy transfer of the liquid, is rather dependent on temperature.

This allows concluding that a significant effect of temperature on the enthalpy transfer coefficient is due to the fact that the resistance to enthalpy transfer of the liquid constitutes a significant fraction of the total resistance.

Next, the technique for the separate determination of mass transfer coefficients in gas and heat transfer in liquid was developed in order to determine the effect of temperature on the fraction of resistance to enthalpy transfer concentrated in the liquid.

The idea of the technique is based on the fact that having conducted several experiments with the same air and brine flow rates (i.e. with constant k_g and α), but different temperatures and finding the ratio $(H^* - H_\mathrm{i})/(t_\mathrm{l} - t_\mathrm{i})$, it is possible to calculate the mass transfer coefficients in gas and heat transfer in the liquid separately. It was also assumed that, $\left(H^* - H_i\right)\big/\left(t_l - t_i\right) \approx \left(\mathrm{d}H/\mathrm{d}t\right)_{t=t_{\text{жс}}}$ where H is the air enthalpy that is in equilibrium with the brine at temperature t.

We performed calculations of the air enthalpy in equilibrium with a saturated sodium chloride solution at different temperatures of the brine, and then the temperature derivative of enthalpy. The results of these calculations are summarized as the following equation:

$$\mathrm{d}H/\mathrm{d}t = 0{,}7 + 0{,}0144\, t + 0{,}00036\, t^2, \qquad (3).$$

The heat transfer coefficient in the liquid and the mass transfer in the air were determined as follows. According to the results of experiments carried out at different temperatures, using the method of regression analysis the values of the coefficients a_0 and a_1 in the linear equation were found

$$1/k_H = a_0 + a_1\, (d\mathrm{H}/d\mathrm{t}), \qquad (4)$$

Comparing equations (4) and (2) and, taking into account the accepted assumption, one can see that $a_0 = 1/k_\mathrm{g}$, and $a_1 = 1/\alpha$. This allows finding the needed values of heat transfer coefficients in liquid α and mass transfer coefficient in gas k_g.

Results of the experiments processed showed that the proportion of liquid resistance in the total resistance to enthalpy transfer in the temperature range studied varies from 18% at 29 °C to 40% at 53 °C.

The represented data shows that the resistance to heat transfer of the liquid in the process of evaporative solution concentration when using in the cooling tower of fall-through trays is as large as when using conventional irrigators. This indicates that an attempt to intensify cooling only by increasing the mass transfer coefficient in the gas, for example, by increasing the air rate, will not have large effect, especially at high temperatures of the cooling solution. The result can be achieved only with simultaneous turbulization of both gas and liquid phase.

The technique of separate determination of the coefficients k_g and α allows studying the influence of the main factors of the enthalpy transfer process on each of these coefficients separately. In particular, to calculate the dependences of these kinetic coefficients on the gas rate in the total cross section of the apparatus w (m/s) and the irrigation density l (m^3/m^2s), the following equations were obtained.

$$k_g = 0{,}82\, w^{0{,}88}\, l^{0{,}85}; \qquad (5)$$

$$\alpha = 17{,}8\, w^{0{,}54}\, l^{0{,}47} \qquad (6)$$

Equations (5), (6) indicate that the gas rate and irrigation density are approximately equal to both the mass transfer rate in the gas and the heat transfer rate in the liquid.

Conclusions

The ratio between the intensity of the mass transfer in gas and the heat transfer in liquid during the evaporative solution concentration in direct contact with air has been studied. It was determined that the share of liquid resistance in the total resistance to enthalpy transfer increases with temperature, increasing in the range from 30 to 50 °C by almost 2 times, and reaches 40%.

The technique has been developed for the separate determination of the mass transfer coefficients in gas and heat transfer in liquid, which makes it possible to study the influence of the main factors of the enthalpy transfer process on each of these coefficients separately. In particular, equations are given for estimating gas rate and irrigation density that impact coefficients mentioned.

The results obtained may be interesting both from the viewpoint of studying the mechanism of enthalpy transfer process and for developing a method for calculating the apparatus for the evaporative solution concentration.

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The influence of the bulk density of the coal blend on the gross calorific value of blast furnace coke

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Abstract – it has been established that increasing the bulk density of the coal blend from 0.8 to 1.15 g/cm^3 leads to an increase in the gross calorific value of blast-furnace coke by 0.05–0.12 MJ/kg.

Keywords – coal, analysis, bulk density, coke, gross calorific value.

Introduction

In work [1] it is noted that the prospects for the development of ferrous metallurgy and the influence that the need for saving energy resources and reducing carbon dioxide emissions have on it depends largely on the technological processes in the production of pig iron and coke. In conditions of limited coking coal resources and increasingly tough environmental legislation, coke and pig iron producers in recent years have joined forces to improve coking technology based on technical requirements for the quality and properties of coke in a blast furnace. About 70 % of all energy costs in the iron and steel industry are accounted for by energy consumption in the iron production system, including about 50 % in blast furnaces, about 15 % in coke production, about 5 % in sinter production and about 1 % in production pellets [2]. This indicates the fact that the production of pig iron has the greatest potential for energy saving in the iron and steel industry, and the processes in blast furnaces and in coke production are characterized by the greatest energy intensity and carbon consumption [3]. In turn, about 55–65 % of the mass of coke burns as fuel in the circulation zone in front of the tuyeres, which indicates the need to increase the carbon content in coke and its heat of combustion.

It is known that the quality of the coal blend and, in particular, its bulk density [4, 5], have a great influence on the quality of the blast furnace coke.

Results

To determine the effect of the bulk density of the coal charge on the value of the gross calorific value obtained from its coke, special studies were conducted.

Four coal blends were compiled, characterized by a different set of quality indicators. Table 1 shows the indicators of their proximate, petrographic and ultimate analyzes, from which it can be seen that they significantly differ in these indicators.

Table 1

Technological properties of the experimental blends

Blend	Proximate and petrographic analysis, %			Ultimate analysis, %				
	A^d	V^{daf}	R_o	C^{daf}	H^{daf}	N^{daf}	S_t^d	O_d^{daf}
1	8.3	27.1	1.06	85.43	4.84	2.14	0.54	7.05
2	8.5	29.0	0.96	84.60	4.93	2.17	0.53	7.77
3	8.2	31.7	0.98	83.69	5.05	2.20	0.50	8.56
4	8.5	33.2	0.84	82.96	5.11	2.26	0.47	9.20

The mixtures were detailed to a content of 100 % class 0–3 mm, compacted to a density of 0.8 and 1.15 g/cm^3, and coked in a 5-kg laboratory furnace. The results of the determination of proximate and calorimetric analyzes of the obtained coke are shown in table 2.

Table 2

Technological properties and gross calorific value of experimental coke

Blend	Bulk density of coal blend, g/cm^3	Proximate analysis, %		Gross calorific value, MJ/kg
		A^d	V^{daf}	Q_s^{daf}
1	0.8	11.7	0.5	32.56
	1.15	10.9	0.5	32.61
2	0.8	11.6	0.5	32.80
	1.15	12.0	0.7	32.92
3	0.8	11.2	0.5	32.88
	1.15	11.6	0.7	32.93
4	0.8	12.0	0.7	32.79
	1.15	12.2	0.6	32.87

Conclusion

Based on the conducted research, it can be concluded that compaction of the coal blend from 0.8 to 1.15 g/cm^3 using coal blends differing in proximate, petrographic and ultimate analyzes results in an increase in the gross calorific value of blast-furnace coke by 0.05–0.12 MJ/kg.

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Research in low-temperature heat pump drying

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***Abstract* – Improving the efficiency of operation of drying units can be obtained by applying heat generating units of heat pump type, in which the waste heat drying agent is utilized. The research is focused on the optimization of the actual heat pump cycle in order to reduce energy consumption in heat pump dryer.**

Keywords – drying, heat pump cycles, heat pump, energy consumption, energy efficiency.

Introduction

Modern convective dryers are characterized by low energy efficiency, which is related to large heat losses with the outgoing drying agent. One of perspective ways to improve the thermal efficiency of convective dryers is the use of the energy-saving equipment such as heat pumps [1, 2].

In heat pump drying the moisture, which is removed, doesn't imposed by a drying agent in the environment and condenses on the cold surface of the evaporator and is given in a liquid form. Perceived evaporator heat of water vapor condensation by the heat pump is transformed to a higher temperature level and is returned to the process of drying, which provides a significant decrease of the specific energy consumption than the traditional dryers and helps to reduce thermal "pollution" of the environment.

The main disadvantage of traditional condensing heat pump dryers is inconsistency of the processes of forced draining of heat carrier in the heat pump and desorption of the moisture from the material in the drying chamber. These dryers' temperature parameters of heat pump cycle and, consequently, the degree of dehydration of drying agent maintained unchanged during the whole period of drying, while the characteristics of heat and humidity of drying material are changed. In this mode, the sufficient speed of the process and optimal energy consumption are not provided throughout the whole period of drying, which leads to unnecessary energy consumption.

The aim of studies is to optimization of heat pump operation to minimize energy consumption during convection drying.

Results and Discussion

In the process of heat pump drying the amount of current energy consumption largely depends on the moisture content of drying agent and its drying temperature conditions in the evaporator of the heat pump: the higher the moisture content and temperature of dehydration, the lower specific energy consumption for the removal of moisture from it [3]. However, the dependence of the intensity of desorption of moisture from the material from the moisture of drying agent is reversible: with the increase of moisture content – drying process slows down.

The results of analytical studies of the heat pump cycle energy performances of heat pump drying process based on thermal and humidity parameters of drying agent were received and the optimum regime parameters of dehydration were defined. It is shown that energy consumption in heat pump drying depends on the moisture content and the temperature of the heat drying agent. The more the heat drying agent is dehumidified, the more energy for moisture removal is consumed. The energy consumption increases dramatically when dehumidification is deeper than d = 15 g/kg d.a. Also, the amount of energy consumption for dehydration increases with increasing drying temperature. Therefore, for heat pump dryers optimum drying temperatures are

50...55 °C. At rational operation modes of the heat pump specific energy consumption for moisture removal can be reduced in 1,3-1,5 times.

It is shown that the recovery of the cold using an air-to-air heat exchanger (recuperator) reduces the current energy consumption during heat pump drying. The waste drying agent, which comes in the heat pump evaporator, is partially cooled by already cooled drying agent in heat exchange. It is allows, depending on the efficiency of the recuperator, to reduce the power imputs in drying by 1,5-2 times.

On the basis of the analysis of technological schemes of convection dryers with heat pumps and the results of analytical studies of heat pump drying processes, the experimental convective dryer with a heat pump system for preparation of heat carrier was developed. And energy-saving technological processes of thermal and humidity treatment of the heat carrier with heat recovery of the waste drying agent are proposed.

On the basis of the experimental data on drying kinetics of plant materials at different drying agent humidity the operational parameters of the heat pump dryer are studied. Decrease in drying agent humidity promotes increase in moving force of mass transfer that results in considerable reduction of drying time. However at the maintenance of low air humidity by the heat pump value of energy consumption is decreased. It takes place, because at low humidity considerable part of cold is used non-productively on cooling of dry air mass.

In the experimental heat pump drying plant the primary energy consumption was reduced to 0,7-0,9 kW·h per kg of removed moisture.

Conclusion

1. On the basis of analytical researches of heat pump cycles modes of moisture removal provided a minimum specific energy consumption for the drying process are determined.

2. The use of research results in the experimental heat pump drying plant has allowed to reduce the primary energy consumption to 0,7-0,9 kW·h per kg of removed moisture.

3. Using of the recuperative heat exchanger allows to reduce energy consumption in drying in 1,5-2 times.

Acknowledgments

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The sunflower seeds oil extraction: the mechanism and kinetics of the process

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Abstract ***–*** ***The results of the research of extracting oil from sunflower seeds by the method of extraction are given. The kinetics and mechanism of the extraction process investigated. It is shown that the process of extracting sunflower seed oil is complicated and include as intra-diffusion and outer-diffusion oil transfer is similar to extraction of target components from other seeds of plant material (amaranth, rapeseed, etc.). The technique of experimental calculation of the diffusion coefficient is given and the slowest stage of the extraction process is determined, which determines the speed of the whole process.***

Keywords – extraction, plant raw materials, mechanism and kinetics of process.

Introduction

The extraction process of target components from plant raw materials is widely used in various industries, especially in food, pharmaceutical, chemical, petroleum, and others. The large demand to agrarian business in Ukraine is a sunflower, which, depending on the natural environment, contains up to 60% of the oil. Sunflower is a base of the agricultural crop because it contains, in addition to oils, protein and other target components which used in the pharmaceutical, chemical, perfumery, and other industries. It should be emphasized that Ukraine exports sunflower oil to over than 100 countries of the world, which requires more efficient technologies for its production for the purpose of providing with world demand.

For today, there are two methods of extracting oil plant raw materials: press and extraction. The advantage of the extraction method is the high degree of oil extraction of 97-98 %, the use of simple equipment and lower energy consumption, compared with the previous method.

The process of extracting the target components from plant raw materials is rather complicated. The complexity of this process is related to the cellular structure of the raw material and the presence of a poorly-permeable shell in the seeds of plants, and also in that, the target component moving within the seed to the surface of the phase contact with the solvent must overcome a number of barriers associated with the complex structure of the seed. The entire process should be considered as intra-diffusion, outer-diffusion and mixed since diffusion is the basis of these processes.

For study and the establishment of a mechanism for the extraction oil process of sunflower seed is used the equation obtained by the method of integral ratios for the extraction processes of the target components from the plant raw material [1-2].

Results and discussion

For a mathematical description of the extraction process adopted the physical model of seed in the form of a ball in the pores of which is the target component, has the form:

$$\tau = \frac{1}{6} - \frac{\varphi_0^2}{2} + \frac{\varphi_0^3}{3} + \varepsilon \cdot \left(1 - \varphi_0\right) + \frac{1}{3 \cdot Bi} \cdot \left(1 - \varphi_0^3\right) \quad (1)$$

For the mixed-diffusion mechanism ($\varepsilon \to \infty$) the equation (1) is reduced to the form:

$$\tau = \frac{t}{T} = \frac{1 - 3 \cdot \varphi_0^2 + 2 \cdot \varphi_0^3 + \frac{2}{Bi} \cdot \left(1 - \varphi_0^3\right)}{1 + \frac{2}{Bi}} \quad (2)$$

The value of φ_0 which corresponds to a certain extraction time t is determined from the material balance:

$$G_0 \cdot (1-\varphi_0) = WC \quad (3)$$

The value of φ_0 changes from 1 to 0 for, for t = 0 °C, φ = 1. To establish the mechanism of extraction, it is necessary to identify the experimental studies of the extraction kinetics in the form of function C = $f(\tau)$.

For the intra-diffusion mechanism, there must be a linear dependence. Such dependence exists, while it is possible to determine the diffusion coefficient – D and the total time T. The diffusion coefficient is determined over the tangent angle of the slope $\Phi = f(t)$

$$D = \frac{R^2 \cdot C_1}{\rho} \cdot tg\alpha \qquad (4)$$

The value of the Bio (Bi) criterion can be determined using the linearization method of equation (1) by introducing a new function y and argument a:

$$y = \frac{1 - \frac{t}{T} \cdot \frac{1}{1-\varphi_0}}{\varphi_0 \cdot (1-\varphi_0)}; \qquad x = \frac{2\varphi_0}{(1-\varphi_0)};$$

then the equation (1) is converted into a linear $y=Ax+B$ (5)

where $A = \frac{1}{1+\frac{6}{\varepsilon}+\frac{2}{Bi}}$; $B = \frac{\frac{2}{Bi}}{1+\frac{6}{\varepsilon}+\frac{2}{Bi}}$

Thus, the technique for determining the Bi criterion and ε is reduced to the transformation of equation (1) into a linear, sequential definition of the constants A and B, from which the criteria of Bi and ε are determined.

Experimentally we investigated the kinetics of extraction of oil from shredding sunflower seeds n-hexane (t = 69 ° C) in Soklet apparatus for different mean grain diameters d_{aver} = 0.7 mm, d_{aver} = 0.5 mm, d_{aver} = 0.25 mm. The research results showed that this process passes by a mixed mechanism (outer- and intra-diffusion mechanism). Also, the value of the diffusion coefficient was determined by equation (4), which is $D = 1.5 \cdot 10^{-12}$ m/s.

Conclusion

Experimentally we investigated the kinetics of extraction of oil from shredding sunflower seeds. The research results showed that this process passes by a mixed mechanism.

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Effect of Support Nature on the Efficiency of B–P–V–W–O_x Catalysts of Acrylic Acid Synthesis with Aldol Condensation of Acetic Acid with Formaldehyde.

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***Abstract* – The catalytic systems of the B–P–W–V–O_x composition have been investigated on different types of supports. The best by the target product yield is the catalytic system of the composition B–P–W–V–O_x/TiO_2 anatase. The optimal conditions for the process are: temperature – 375 °C; residence time – 8 s, at which acetic acid conversion is 63.8 %, acrylic acid selectivity – 92 % and acrylic acid yield – 58.8 %.**

Keywords – acrylic acid, aldol condensation, solid catalysts, nature of support.

Introduction

The most valuable representatives of acrylate monomers are acrylic acid and its derivatives, which are the main source material for the production of most acrylic polymeric and composite materials. One of the most promising methods for the production of acrylate monomers is the aldol condensation of carbonyl compounds. A significant advantage of this method is the possibility of using widely available raw materials such as natural gas and coal. The simplicity of technological design and the small number of stages of the process determine the economic and technological feasibility of using this method for the production of acrylate monomers [1, 2]. In previous studies [3] it has been established that the catalyst of the composition B–P–V–W–O_x/SiO_2 shows high efficiency in the gas-phase condensation of acetic acid with formaldehyde to acrylic acid and that the porous structure of the catalyst has significant influence on its activity [4]. It is known that the support can also affect the process. For these reasons, the developed active catalyst phase (B–P–V–W–O_x) is deposited on a supports of different nature with similar parameters of porous structure (pore diameter of about 10 nm, specific surface area of 200-250 m^2/g): SiO_2, TiO_2 anatase, ZrO_2, SnO_2–TiO_2, Al_2O_3. To provide equivalent parameters of the porous structure for all supports, they were pre-treated with hydrothermal methods (hydrothermal treatment (HTT) or mechanochemical treatment (MChT)).

Thus, the purpose of this work is to investigate the effect of the nature of the support of B–P–V–W–O_x catalysts in the synthesis of acrylic acid by the aldol condensation of acetic acid with formaldehyde.

The influence of different types of mesoporous supports for B–P–V–W–O_x catalysts, namely: SiO_2, SiO_2 (HTT at 150 °C, 3h), SnO_2–TiO_2, Al_2O3, TiO_2 anatase with $TiO(OH)_2$, Al_2O_3 (MChT in H_2O at 300 rpm), TiO_2 anatase with $TiO(OH)_2$ (MChT in H_2O at 300 rpm) and $Sn(OH)_4$–TiO_2 (MChT at 600 rpm) on their efficiency in the process of aldol condensation of acetic acid with formaldehyde to acrylic acid. The list of synthesized catalysts is given in Table 1.

Various methods of preparation of catalysts and their influence on the main parameters of the process (Table 1) are also investigated in this work.

Table 1

Catalysts of aldol condensation of acetic acid with formaldehyde

№	Components of the active phase	The support and parameters of its modification	Preparation method
K_1	B–P–V–W–O_x	SiO_2	Impregnation with evaporation
K_2		SiO_2 (HTT at 150 °C 3h)	
K_3		SnO_2-TiO_2 (MChT at 600 rpm)	
K_4		Al_2O_3 (MChT in H_2O at 300 rpm)	
K_5		TiO_2 anatase (MChT in H_2O at 300 rpm)	
K_6		SiO_2	Impregnation without evaporation
K_7		SiO_2 (HTT at 150 °C 3h)	
K_8		SnO_2-TiO_2 (MChT at 600 rpm)	
K_9		Al_2O_3 (MChT in H_2O at 300 rpm)	
K_{10}		TiO_2 anatase (MChT in H_2O at 300 rpm)	

It has been established that for a series of catalysts prepared by the method of impregnation without evaporation, the best catalyst for the selectivity of the formation of acrylic acid is K_5 (TiO_2 anatase/B–P–V–W–O_x) (Fig. 1). The catalyst K_5 shows the following results at 375 °C and the residence time 8 s: OK conversion is 51.8 %, AK selectivity – 94.5 %, AK yield – 48.5 %.

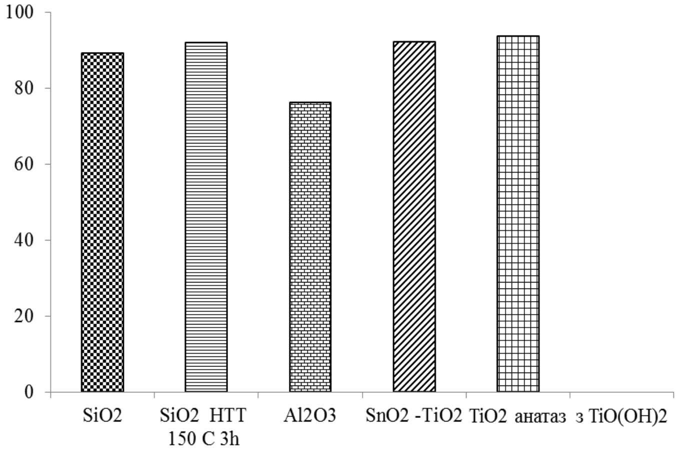

Fig. 1. Comparison of the selectivity of the AK formation on the catalysts K_1–K_5, temperature 375 °C, residence time 8 s.

And for a series of catalysts prepared by the method of impregnation with evaporation, the best catalyst in the process of aldol condensation is K_{10} (TiO_2 anatase MChT H_2O at 300 rpm) (Fig. 2). The catalyst K_{10} shows the following results at 375 °C and residence time 8 s: OK conversion is 63.8 %, AK selectivity is 92 % and AK yield is 58.8 %.

The comparison of the conversion of acetic acid, the selectivity and the yield of acrylic acid on the best catalyst, namely K_{10}, prepared by impregnation with the evaporation of the active phase solution, with the K_5 catalyst, prepared by the method of impregnation without evaporation, is shown in Fig. 2. The catalyst K_{10} shows better results at 375 °C and residence time 8 s: OK conversion is 63.8 %, AK selectivity – 92 %, and AK yield – 58.8 %. When using the K_5 catalyst, the OK conversion is 51.8 %, AK selectivity – 94.5 %, and AK yield – 48.5 %.

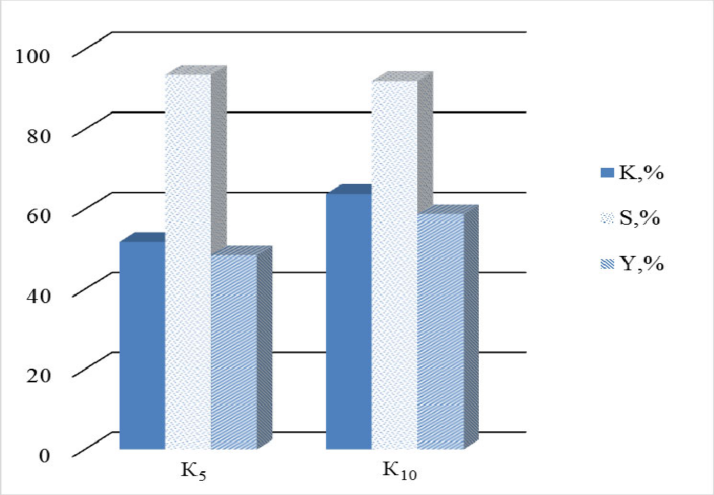

Fig. 2. Comparison of catalytic activity of catalysts (K_5 using as support of TiO_2 anatase and K_{10} using as support TiO_2 anatase MChT H_2O at 300 rpm) synthesized by various methods.

Consequently, not only the nature of the support affects both the catalytic properties of catalysts of aldol condensation of acetic acid with formaldehyde, but also the method of catalysts preparation (impregnation with or without evaporation). The most effective in the process of acrylic acid production is the catalytic system B–P–V–W–O_x/TiO_2 anatase, prepared by impregnating the support with a solution of active phase components, followed by evaporation.

Conclusion

New high-performance catalytic systems, based on a mixture of boron oxides, phosphorus, vanadium and tungsten deposited on SiO_2, SnO_2–TiO_2, Al_2O_3 and TiO_2 anatase, have been devoloped for the process of acrylic acid production using the method of aldol condensation of acetic acid with formaldehyde. It has been established that all developed catalytic systems of the B–P–V–W–O_x composition deposited on a support with a pore size of about 10 nm have high efficiency in the process of aldol condensation of acetic acid with formaldehyde. It is shown that the method of preparation of catalysts (impregnation with or without evaporation) and the nature of the support affects the efficiency of catalysts. The best method is based on the impregnation of the support with the solution of the active phase components with subsequent evaporation; the best support for the B–P–V–W–O_x active phase is TiO_2 anatase.

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Diffusive Transfer During Filtration Drying of Sunflower Stalks

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Abstract – Filtration method for drying rough-stalked agricultural wastes that can reduce power inputs of solid biofuel production has been studied. Diffusive mass transfer has been studied during drying of grinded sunflower stalks to produce fuel briquettes. The temperature effect on effective diffusion coefficient has been examined.

Keywords – rough-stalked agricultural wastes, grinded sunflower stalks, diffusive mass transfer, filtration drying, prism-shaped particles, effective diffusion coefficient.

Introduction

The demand for alternative energy sources in Ukraine increases with rising fossil fuel prices. The country's potential capacity from biomass resources is great. Manufacturing of fuels from plant materials is a prospective direction for Ukraine. Lignocellulosic agricultural wastes are highly abundant in nature. Rough-stalked agricultural wastes are a great part of biomass resources. Sunflowers are already used for oil production, but they can be used as bio-energy plants. They grow as tall as 3 – 4 meters, that's why there are significant amounts of cellulosic biomass which can be converted into solid biofuel with high calorific value. Lignocellulosic material from agro-industrial wastes is a combination of cellulose, hemicellulose and lignin. The stalk composition (%) is: cellulose – 41.8; hemicellulose – 21.3; lignin – 20.1 The high concentration of above-mentioned compounds defines highcalorific power of biofuel made from plant raw material. The technology of solid fuel production from this type of material provides stages of preliminary grinding and drying to humidity of 4–12 % favorable for sustainable briquetting and quality characteristics of received briquettes.

As a result of stalks grinding, the particles with fibrous structure are formed. The particles have prism shape with averaged size of 1.37x1.91x7.14 mm. The initial average moisture content of the investigated sunflower stalks is 60 %. The share of costs for drying is significant in the manufacturing cost of the fuel because modern dryers used now to produce solid biofuels are energy intensive, large and require the installation of treatment equipment. All these facts correspondingly increase the cost of the finished product. We propose the filtration method that can reduce power inputs of solid biofuel production. Recent studies have demonstrated that filtration dryers are energy-efficient and environmentally friendly. Filtration drying of dispersed materials, in particular grinded rough-stalked matter, is a complex process involving mass and heat transfer. During filtration drying the moisture transfer is defined by regularities of both external and pore diffusion.

The aim of the work

The aim of the work is to study the kinetics and the diffusion processes occurred during filtration drying of grinded sunflower stalks.

Experimental study and its analysis

The experiments were carried out at the laboratory plant. To study the diffusion processes occurred during filtration drying of grinded sunflower stalks the layer with the height H = 40R was formed (R – the defining size of prism-shaped particle). A container with a sample was placed into a drying installation. Heat agent with the temperatures of 293, 316, 333, 353 and 373 K was filtered through the sample layer. Heat agent flow rate was constant. The experiments were carried out till the material weight became constant. The temperature was controlled by RT-0102 thermoregulator), the sample weight was measured using Axis AD3000 electronic scales.

We studied the kinetic peculiarities of grinded sunflower stalks filtration drying at different temperatures of the heat agent.

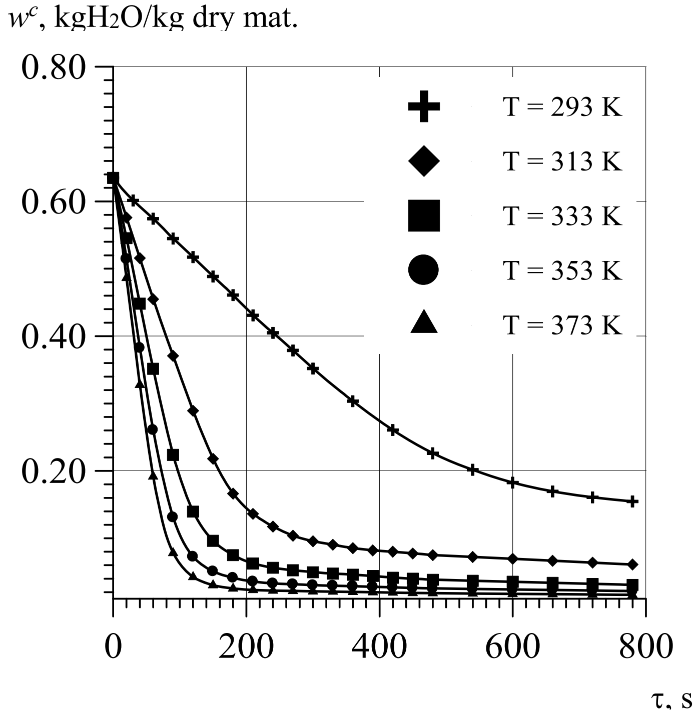

Fig. 1. Kinetics of grinded sunflower stalks drying at different temperatures of heat agent (H = 0.06 m; □0 = 1.71 m/s).

The upper limit is such temperature, under which spontaneous ignition does not occur. The experimental results are represented in Fig. 1. The kinetic curves are characterized by long period of partial saturation of the heat agent by moisture. This fact indicates the proceeding of pore-diffusion processes in the material particles which define the time of filtration drying. Recent studies have demonstrated that the increase in heat agent temperature intensifies the drying process. The values of final moisture content (wfc) achieved at process time of 600 s are given in Table 1.

Table 1

Moisture content of grinded sunflower stalks at drying time of 600 s

T, K	293	313	333	353	373
w_f^c, kgH$_2$O/kg dry mat.	0.183	0.071	0.035	0.024	0.017

The temperature effect on effective diffusion coefficient has been examined. The values of Dw* are represented in Table 2.

Table 2

Dependence of effective diffusion coefficient on the heat agent temperature

T, K	293	316	333	353	373
$D_w^{*}\cdot10^8$, m^2/s	1.056	4.156	6.749	9.291	13.474

Overall, the results show that the increase of heat agent temperature increases the temperature inside the particles and saturation vapor pressure over the liquid surface and thus intensifies the diffusion processes. The graphic dependence Dw* = f(τ) is plotted on the basis of results from Table 2 (Fig. 2).

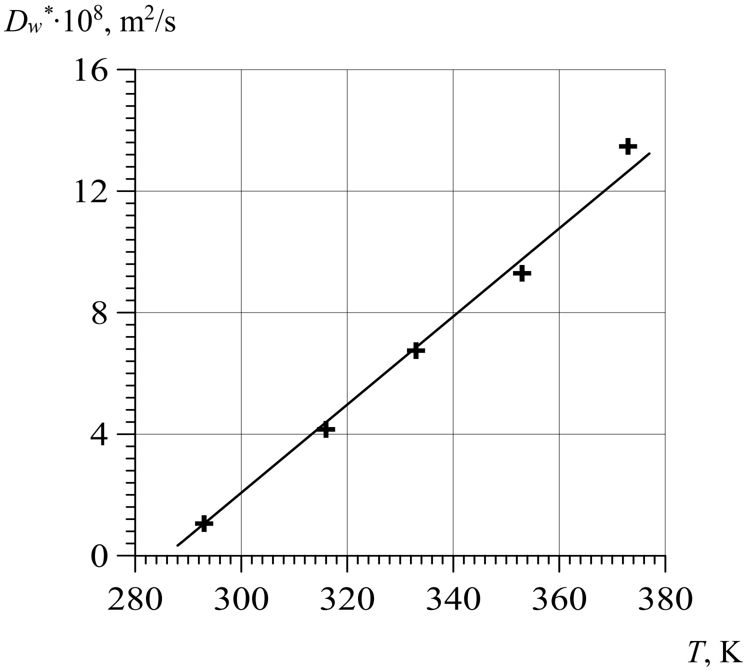

Fig. 2. Effective diffusion coefficient Dw* vs. the heat agent temperature.

Conclusions

As the result of these research studies, the estimated dependence of the effective diffusion coefficient on the heat agent temperature is approximated by equation:

$$D_w^t = D_w^{293} + 1.45\cdot10^{-9}(T-293) \quad (1)$$

The deduced equation allows to calculate theoretically the effective diffusion coefficient for the grinded sunflower stalks within temperature range of 293–373 K.

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Investigation of oxygen chemisorption during regeneration of a quinhydrone absorbing solution in continuous barbotage layer absorbers

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Abstract – The results of investigations of air oxygen chemisorption during regeneration of a quinhydrone absorbent solution in apparatus with a continuous barbotage layer are given. It is shown that the chemical reaction between chemisorbed O_2 and quinhydrone catalyst reducing form is rapid and occurs in a liquid film. Researching results can be used for the choice of mass-exchange equipment for the process.

Keywords – oxygen sorption; absorbing solution, quinhydrone, barbotage layer; acceleration coefficient.

Introduction

The quinhydrone method of gases purification from hydrogen sulfide is based on the removal of H_2S from gases by an alkaline solution of the quinhydrone catalyst [1]:

$$Na_2CO_3 + H_2S \Leftrightarrow NaHS + NaHCO_3, (1)$$

$$NaHS + \{Q\} + NaHCO_3 = S\downarrow + Na_2CO_3 + \{Q\}H_2, (2)$$

$$\{Q\}H_2 + \tfrac{1}{2}O_2 = \{Q\} + H_2O, (3)$$

where $\{Q\}$ and $\{Q\}H_2$ are oxidizing (quinone) and reducing (hydroquinone) forms of the catalyst.

Equation (3) describes the chemisorption process of the solution regeneration, which consists of two stages - the absorption of air oxygen by the absorbent solution and the interacting of the reducing form of the quinhydrone catalyst with absorbed oxygen. For the regeneration of absorbing solutions with air oxygen in similar industrial processes of gases purification from hydrogen sulfide (Lo-Cat, Stretford, Takahaks, Thylox, Unisulf, etc.), as a rule, use absorbers with a continuous barbotage layer [2]. The effectiveness of the use of this type of apparatus for the quinhydrone method is not established. Therefore, it became necessary to carry out studies on chemisorption of air oxygen by quinhydrone absorbing solution in this type of absorbers.

The aim of the research was to determine the acceleration coefficient of absorption in the process of oxygen chemisorption from the air in apparatus with a continuous barbotage layer.

Experimental part

The research was carried out in a laboratory installation, the main apparatus of which was a glass column (internal diameter of 0.035 and height of 0.5 m) with a built-in bubbler (a porous glass plate with a thickness of ≈5 and a pore size of 0.2 ... 0.6 mm) in the lower parts of the column.

For investigations of the acceleration coefficient of absorption of air oxygen was carried out the two series of experimental studies, which was differed in the type of absorbing solution - soda (10 kg/m^3 Na_2CO_3) or quinhydrone (10 kg/m^3 Na_2CO_3 and 5 kg/m^3 quinhydrone). The other parameters were constant: temperature – 17 ^oC; the height of the solution in the column - 0,25 m. Air flow varied within $(0.78 ... 1.83)\cdot 10^{-6}$ m^3/sec. Duration of absorption of oxygen was 480 sec and chemisorption 3600 sec. The dissolved oxygen was stripped from the soda solution by boiling before the investigation. The dissolved oxygen concentration in the solution was determined by Winkler's method. The quinhydrone solution before the studies were saturated with H_2S to reach its concentration of 0.85 kg/m^3. The amount of chemosorbed oxygen was calculated based on analyzes results of the amount of oxidized H_2S in the solution.

To calculate the acceleration coefficient of absorption χ [3], the ratio of the multiplication of the liquid phase mass transfer coefficients in the chemisorption (β_L^{chem}) and absorption (β_L^{abs}) processes on the surface of the contacting phases (F_i) were used

$$\chi = \frac{\beta_L^{chem} \cdot F_i}{\beta_L^{abs} \cdot F_i} = \frac{\beta_L^{chem}}{\beta_L^{abs}} \ . \ (4)$$

For calculations of the multiplications in these processes, the basic mass transfer equation [3] was used, in which, in view of the results [4], neglected the diffusion resistance of the gas phase.

Results and discussion

Studies and calculations for the two series showed (Table) that, with increasing air flow, the multiplication of the mass transfer coefficient from the liquid phase on the surface of the contacting phases ($\beta_L \cdot F_i$) increases slightly for both absorption and chemisorption processes. The degree of absorption and chemisorption of the oxygen increases with decreasing of the air flow. However, for the chemisorption process, it is an order of magnitude larger.

Table

Investigation results of the influence of air flow on the processes of the air oxygen sorption

№	Air flow, V_{air}, m^3/sec	Amount of O_2 in the air, N, mole	Degree of sorption, %	Average driving force of sorption, Pa	Rate of sorption, $\Delta N/\tau$, mole/sec	Multiplication, $\beta_L \cdot F_i$, (m/sec)$\cdot$m^2
Absorption process						
1	$0.78 \cdot 10^{-6}$	$3.51 \cdot 10^{-3}$	0.79	17224	$5.78 \cdot 10^{-8}$	$22.85 \cdot 10^{-8}$
2	$1.05 \cdot 10^{-6}$	$4.73 \cdot 10^{-3}$	0.63	16920	$6.17 \cdot 10^{-8}$	$24.84 \cdot 10^{-8}$
3	$1.40 \cdot 10^{-6}$	$6.30 \cdot 10^{-3}$	0.48	16830	$6.35 \cdot 10^{-8}$	$25.71 \cdot 10^{-8}$
4	$1.56 \cdot 10^{-6}$	$7.02 \cdot 10^{-3}$	0.47	16668	$6.89 \cdot 10^{-8}$	$28.15 \cdot 10^{-8}$
5	$1.83 \cdot 10^{-6}$	$8.24 \cdot 10^{-3}$	0.40	16775	$6.95 \cdot 10^{-8}$	$28.21 \cdot 10^{-8}$
Chemisorption process						
6	$0.78 \cdot 10^{-6}$	$2.64 \cdot 10^{-2}$	5.11	20042	$3.74 \cdot 10^{-7}$	$116.54 \cdot 10^{-8}$
7	$1.05 \cdot 10^{-6}$	$3.54 \cdot 10^{-2}$	4.29	20209	$4.23 \cdot 10^{-7}$	$129.91 \cdot 10^{-8}$
8	$1.40 \cdot 10^{-6}$	$4.72 \cdot 10^{-2}$	3.54	20332	$4.63 \cdot 10^{-7}$	$142.43 \cdot 10^{-8}$
9	$1.56 \cdot 10^{-6}$	$5.26 \cdot 10^{-2}$	3.53	20365	$5.17 \cdot 10^{-7}$	$158.77 \cdot 10^{-8}$
10	$1.83 \cdot 10^{-6}$	$6.18 \cdot 10^{-2}$	3.17	20441	$5.44 \cdot 10^{-7}$	$166.44 \cdot 10^{-8}$

Calculations have shown that the acceleration coefficient of the absorption χ = 5.10 ... 5.90 (χ_{aver} = 5.48), and the parameters [3] M = 9.95 and R = 7.04. The obtained values of $M>R>>1$ and χ = 5.48 indicate that the reaction between the dissolved oxygen and the reducing form of the catalyst is rapid and ends in a liquid film, and the partial oxygen pressure over a quinhydrone solution which containing chemosorbed H_2S, is zero [3].

Conclusion

In an apparatus with a continuous barbotage layer, the diffusion resistance of the liquid film during the oxygen chemisorption is large, which prevents the desired rate of the solution regeneration. Therefore, this type of mass-exchange equipment we do not recommend to regenerate the absorbing solution of the quinhydrone method of gases purification from hydrogen sulfide.

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Obtaining Modified Bitumen Rubber Crumb for Cold-Rolled Roofing Materials

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***Abstract – The method of obtaining a bituminous composition, which can be used in the manufacture of cold-applied roofing materials using rubber crumb, is developed. The optimum content of components of a three-component bitumen composition is established*.**

Keywords – bitumen, bitumen composition, linseed oil, roofing materials, rubber crumb

Introduction

Roofing materials based on bitumen are very common in the Ukrainian market. Soft roof is widely distributed on the area of cottage houses and industrial buildings. The undoubted advantage is its complete dispersion to corrosion and decay. Moreover, meat tastes have excellent thermal insulation qualities. And thanks to the small weight, a soft roof can even be used to cover light wooden structures.

Roofing materials must have durability, water resistance, heat resistance and be resistant to atmospheric influences [1]. Also, they must be elastic enough to prevent cracks and tears from occurring due to shrinkage, temperature and other deformations of the insulated constructions. Nowadays, all the more popular are roofing and insulating materials of cold drawing. The advantage of these materials is a short lead time and ease of installation.

Bitumen from which roofing materials are made are very sensitive to temperature fluctuations and various atmospheric influences, especially to ultraviolet rays. Their negative property is low frost, which makes the coating short-lived. Although bitumen materials are the cheapest, but because the life of such a roof does not exceed 5-7 years and the total cost of supporting the roof in order for 30-40 years is quite significant. The disadvantage of well-known today's cold-drawing materials is the lack of adhesion, poor high temperature and low temperature properties [2].

Experimental

The first stage in the production of cold-drawn bituminous materials was the study of the characteristics of the binary mixture "bitumen: linseed oil". Flaxseed oil was chosen as a component of bitumen composition, which would provide the necessary adhesive and plastic properties.

Bitumen from which roofing materials are made are very sensitive to temperature fluctuations and various atmospheric influences. Their negative property is low frost, which makes the coating short-lived. We have studied the possibility of developing bitumen material which can be used for the production of cold-applied roofing materials. Thus, the second stage in the production of cold-drawn bituminous materials was the study of a three-component bituminous composition "bitumen BNB 70/30 : linseed oil : rubber crumb". As the third component, used rubber crumb, which is obtained by crushing exhaust tire.

The study of the temperature dependence of the softening of a three-component mixture from its composition demonstrated the mutual influence of the components.

It has been established that with the increase in the content of rubber crumb and the decrease in the content of linseed oil in the mixture, the softening temperature rises. It is also established that reducing the content of flaxseed oil and increasing the amount of rubber crumb in the mixture leads to a decrease in its penetration. The ductility of a three-component mixture increases with increasing flax content.

Maximum elasticity is achieved with the highest content of rubber crumb and the minimum amount of linseed oil. Studies have established that the flexibility at -25°C is maintained at the content of flax oil in a mixture of more than 15% by weight, and the amount of rubber crumb to 12.5% by weight.

If these requirements are not met, the bituminous material becomes fragile, which does not meet the requirements. It is also established that adhesion decreases with the addition of rubber crumb in all cases.

Analyzing the obtained results, an optimal composition of the three-component bitumen composition, which meets all the requirements for cold-rolled roofing bitumen, was determined. It was established that the content of bitumen BNB 70/30 in this composition should be 65.0-78.5% by weight, the content of linseed oil - 12.5-22.5% by weight, the content of rubber crumb - 9.0-12,5% by weight.

Based on the obtained results, a bituminous composition for cold-drawing materials was obtained, consisting of 72.5% by weight. bitumen grade BNB 70/30, 17.5% by weight linseed oil and 10.0% by weight of rubber crumb. Characteristics of such a composition are shown in Table.

Table 1

Characteristics of a bituminous composition for cold-rolled roofing material

Index	Values	Requirements for bitumen composition
Softening temperature, C	76,0	> 70
Ductility at 25 °C, cm	3,2	–
Penetration at 25 °C, 0.1 mm	33,0	–
Elasticity, %	53,0	–
Low-temperature flexibility at at -25 °C	stands the test	stands the test
Heat resistance at 60 °C	stands the test	stands the test
Adhesion, N/cm^2	5,6	> 5.0
Water absorbing, %	0,15	< 1.0

Conclusion

On the basis of the results of the study of the dependence of the properties of three-component systems, a new type of bituminous composition for cold-applied roofing materials was obtained. The developed bitumen composition for cold-rolled roofing material using rubber crumb also meets the requirements set by us. Due to the elevated temperature softened, the roofing materials developed have high resistance in hot climatic conditions. Also, the optimal composition of the three-component bitumen composition was determined from the obtained results.

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Investigation of the condition of non-stationary process during the dissolution of a set layer of granular material

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Abstract* – *The dissolution of a stationary set layer of a granular material was investigated. The method of experimental research of dissolution was presented, the coefficient of mass deducing, the value of which was used during the analysis of dissolution of the layer, was determined. The change in concentration over the height of the layer, depending on the time, was theoretically determined.

Keywords – granular material, dissolution, filtration, layer.

The dissolution of solid substances in industry is realized by various methods: dissolution in a device with mechanical or pneumatic mixing, in devices with a fluidized bed of granular material, in auger solvents and devices with set and moving solid phase. The latter method is called dissolution in the stationary layer, through which the liquid phase is filtered. The dissolution of solid substances by filtration through a layer of granular material is realized in the natural environment during precipitation. Water with dissolved salt in it is collected in underground storage facilities and is used for water supply needs of the population. The mathematical models of dissolution presented in the literature refer to stationary or quasi-stationary processes in a layer of granular material. In reality, the initial stage of dissolution is always non-stationary and the nature of the change in the size of the particles over the height does not correspond to the stationary dissolution process.

Experimental researches in a layer were conducted in a glass column, which in the bottom part contains a grid, which was filled with a fraction of sodium chloride salt. Distilled water was supplied from above and its flow was regulated by a crane. After passing the column, the liquid was collected in a measuring cup. In the first series of experiments, the coefficient of mass deducing during the dissolution of a solid substance in the stationary layer was experimentally determined and its comparison with the theoretical values calculated according to the criterion equations was carried out. The value of the coefficient of mass deducing β was determined according to the dependence representing the averaged value on the height of the layer, and was equated to the theoretical value determined according to the criterion equations. The determined value of the coefficient of mass deducing on the basis of experimental data is $1{,}34 \cdot 10^{-5}$ m/s, and the theoretical - $2{,}12 \cdot 10^{-5}$ m/s, which is explained by the fact that the particles that are in the layer contact with each other and this surface does not take part in mass transfer.

The calculation of non-stationary dissolution of the stationary layer is presented. The height of the layer was divided into separate layers, each of which was equal to the initial diameter of the salt particles. The initial condition was the zero concentration of liquid entering the upper layer of the granular material. The kinetics equation of the dissolution was used and the time of complete dissolution of the upper layer of particles T_S was determined.

Dividing the mass on the volume of the liquid, which contacts with the first layer, we determine the average concentration that leaves the first layer and is the initial concentration for the second layer c_1. For any *i*-th layer, which is multiple to the initial particle diameter, the time of its complete dissolution τ_i will be greater than the T_S due to the reduction of impellent of the process.

Graphical dependence of the relative diameter of solid particles on the height of the layer is presented. Altitude is measured on top of the device. The calculation data are given for the time of complete dissolution of the upper layer, which for the conditions of the experiment is 322 seconds.

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Continuous Improvement in Education of Chemical Engineers and Researchers in the United States

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Abstract* – *The education of young chemical engineers and scientists in the United States is an ongoing process of mutual improvement of universities and industry enterprises. Approaching education to business needs ensures the success of graduates and enterprises, increases the quality of education, influx of students, and the prestige of the university.

Keywords – education, training, skill, chemical, engineer, scientist, internship, co-op, bachelor, master.

Introduction

The success of the professional activities of young specialists in the field of chemical engineering and science is closely linked to the level and quality of their training at universities and workplaces. Some steps and requirements for the education and training of students and young professionals in their profession and the mutual influence of professional knowledge and skills on the education process are discussed below.

Education and Training of Young Chemical Engineers

Undergraduate Education

Professional career of chemical engineers begins from earning a bachelor's degree in Chemical Engineering [1].

Some of the steps that young chemical engineers and scientist must do to earn a Bachelor's Degree Chemical Engineering, are as follows:

1. Education at Leading Universities

When hiring new college graduates, recruiters from the large oil and chemical companies are focusing their efforts at only few but top-rated educational institutions in the field of Chemical Engineering.

One of the leaders in the teaching of chemical engineering in the Midwest of the United States, the Department of Chemical and Biomolecular Engineering (CHBE) of the University of Illinois at Urbana-Champaign, for example [2], offers classes in chemical engineering that include, but are not limited to, the following:

1) Principles of Chemical Engineering

Material and Heat Balances.

2) Chemical Engineering Thermodynamics

Fundamental concepts and the laws of thermodynamics; the first and second law applications to phase equilibrium and chemical equilibrium and other applications in the Chemical Engineering profession.

3) Individual Study.

Individual study of problems related to Chemical Engineering for sophomores, juniors, & seniors.

4) Momentum & Heat Transfer

Introduction to fluid statics and dynamics; dimensional analysis; design of flow systems; introduction to heat transfer; conduction, convection, and radiation.

5) Mass Transfer

Introduction to mass transfer processes and design methods for separation equipment.

6) Chemical Reaction Engineering

Chemical kinetics; chemical reactor design; the interrelationship between transport, thermodynamics, and chemical reaction in open and closed systems.

7) Analysis of Data

Nature of probabilistic models for observed data; discrete and continuous distribution function models; inferences on universe parameters based on sample values; control charts, acceptance sampling, and measurement theory.

8) Unit Operation Laboratory

Experiments and computation in fluid mechanics, heat transfer, mass transfer, and chemical reaction engineering.

9) Process Design

Capstone design course where students apply principles from previous courses to the design of complete chemical process systems. Topics include: techniques used in the synthesis and analysis of chemical processes, process simulation and optimization, effective communication in a chemical process engineering environment.

10) Process Control & Dynamics

Techniques used in the analysis of process dynamics and in the design of process control systems. Laplace transforms[1], stability analysis, and frequency response methods.

11) Chemical Kinetics & Catalysis

Problems in chemical kinetics; techniques for the prediction and measurement of rates of reactions; homogeneous and heterogeneous catalysis chain reactions.

12) Projects

Laboratory; development of an individual project.

High scores in professional subjects place a student on the top of a list of job candidates.

Scores below ‘B’[2] in the above-mentioned disciplines significantly reduce the student's chances of getting a job in a large oil / chemical company.

Also important are good marks on such universal subjects as chemistry, mathematics, physics and physical chemistry.

2. Internships & Co-ops[3]

While in the university, in order to graduate and gain work experience, a student must complete multiple internships & co-ops.

In the vast majority of cases, large oil and chemical companies, while hiring young professionals, offer jobs to students before their graduation, most often, after the co-op during the final year of education.

As a rule, a student must complete at least 2-3 internships and cooperatives during his/her studies. To apply for the internship, the applicant must submit his/her Curriculum Vitae (CV)[4] . Resumes are also acceptable.

During the internships and co-ops, a student must undergo the necessary training, complete a series of individual tasks, and demonstrate that he/she has not only the knowledge and skills necessary for the successful completion of job assignments immediately after hire, but also

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[1] The purpose of the Laplace Transform is to transform ordinary differential equations (ODEs) into algebraic equations, which makes it easier to solve ODEs [3].

[2] The range of grades A (A+,A, A-) corresponds to 90-100%, or 3.67-4.0 GPA (grade point average); B (B-, B, B+) corresponds to 80-89%, or 2 .67–3.66 GPA score [4], [5].

[3] Cooperative education programs, commonly referred to as co-ops, and internships both provide students with the opportunity to gain work experience in their career fields. Students who participate in co-ops stop taking classes to work full time. Co-ops are typically paid and last anywhere from three to 12 months [6].

[4] A curriculum vitae (CV) provides a summary of your experience and skills. Typically, CVs for entry-level candidates are longer than resumes – at least two or three pages. The CVs include more information than resumes, particularly details related to one's academic and research background [7]

positive attitude towards colleagues, persistence and interest in the work he/she performs. Outstanding final presentation summarizing the work done during the internship / co-op as well as excellent characteristics of the working professionals who observe and teach students during internships/ co-op are mandatory.

The list of works of practical importance for oil refineries and chemical enterprises and laboratories, which are performed by students during internships and cooperatives, is not short. Competition in the oil and chemical industries forces oil and chemical companies to use all available resources in order to continuously improve the quality of their products, optimize chemical processes, equipment, machines, catalysts, etc., including the use of students to achieve the company’s goals.

Internships and cooperatives, in turn, improve the level of on-campus education. When students who were professionally trained by industry experts return back to universities to continue their education, together with new knowledge and skills, they bring new and elevated requirements to their lecturers and instructors to the content and quality of the classes.

A student must always consider internships and co-ops as the main and in the most cases the only way to learn and improve professional skills needed to obtain an attractive job offer and succeed at work in the future.

The equally important result of internships and co-operatives is that out-of-campus education helps the student to strengthen or change (in some cases) his/her choice of future profession. The student needs to be sure that the work he/she devotes about a third of his/her active life is important, attractive and rewarding. When you study at a college, particularly at a junior level, it's never too late to make up your mind and change your future profession.

3. Development of Professional Skills

During the university years and early in his/her job career, a young professional must gain not only certain knowledge, but also develop and master skills needed to succeed. Some of skills listed below are mentioned in [1]:

1) Knowledge of organization's behavior, it strengths and weaknesses, risks and opportunities
2) Skills to think analytically to find potential problems and develop solutions
3) Ability to work creatively and think innovatively
4) Ability to solve problem when problem arise
5) Management skills to lead the teams of engineers and skilled workers
6) Teaching and mentoring skills
7) Ability to stay calm and work in emergencies
8) Ability to work under the constant stress
9) Ability to work in multicultural environment
10) Excellent oral and written communication skills
11) Computer skills (e.g. MS Office package, Adobe Acrobat Professional, Adobe Access, Dell Statistica, etc.)
12) Process and equipment simulation software (e.g. KBS Petro-Sim Suite, Aspen HYSYS for oil & gas processing engineers, Aspen Plus for chemical engineers)
13) Unit health monitoring and performance analysis software & tools (e.g. MS Visual Basic, MathWorks Matlab, PTC MathCad, MS Excel, Aspen HYSYS, KBS Petro-Sim Suite, OSIsoft PI ProcessBook, DataLink, etc.)
14) Foreign languages

4. Graduation with B.S. in Chemical Engineering.

Preferred scores are *summa cum laude* -GPA[5] 4.0+; *magna cum laude* -GPA 3.8 to 3.9; *cum laude* –GPA 3.5 to 3.7. Avoid GPA below 3.0.

Students who graduate from the university not only in their major in Chemical Engineering but also obtain a second (minor) degree in the related to chemical engineering practices (e.g. Material Science, Chemistry, Math, Computer Science, etc.), have a significant competitive advantage.

Education and Training after Obtaining a Bachelor's Degree

Professional Education and Training at Universities

Education and training of recent graduates and working professionals continue in specialized programs at universities and in specialized professional organizations.

The Professional Master’s Program (PMP) and **Doctor of Philosophy (Ph.D.) Program** are the most commonly forms of professional education offered by universities.

1. Professional Master’s Program

The Professional Master’s Program aims to provide advanced technical and management training to aspiring industrial leaders in chemical engineering and to prepare graduates for specialized careers in industry, academia, and government.

The Charles D. Davidson School of Chemical Engineering at Purdue University, US, for example, offers the full time, 12 – 16 month, non-thesis M.S. program to a recent graduate of a STEM[6] program or a current professional [8].

During this program, students have the option to maximize their business and management component and may opt to pursue the MSChE[7] + MBA[8] dual degree option.

2. Doctor of Philosophy Program

The Doctor of Philosophy Program is designed to prepare each student to take an active part in the development and growth of the field of chemical engineering at all levels in academia, industry, and various research organizations [9]. All admitted graduate students must demonstrate competence in graduate course work and demonstrate the capability to do independent research.

Like internships and cooperatives, recent graduates and industrial engineers' professional education improves higher education at universities. When an experienced engineers returns from industry and laboratories to universities to continue studying at M.S. or Ph.D. programs, because of the work they perform at universities (for example, by teaching some classes or helping students conducting laboratory research), they bring their professional knowledge and experiences into the learning process enhancing the content and quality of teaching.

3. Online Degrees and Certificates

Working adults, chemical engineers and scientists who want to prepare for better career opportunities, have the opportunity to learn and graduate on-line. The Department of Online Professional Certification Programs at Purdue University, for example, offers numerous graduate programs and certifications in business administration, management and leadership, project management, etc. [10].

Education and Training in Professional Societies

Less common but valuable form of continuous education for students, engineers, and scientists is education and certification in professional societies.

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[5] According to the USA most common higher education grading system, ‘Normal courses’ are graded with GPA score up to 4. ‘Honor courses’ are graded with a GPA score up to 5 [4], [5].

[6] STEM- Science, Technology, Engineering and Mathematics, is a term used to group together these academic disciplines.

[7] MSChE- Master of Science In Chemical Engineering

[8] MBA- The Master of Business Administration

There are multiple professional societies in the field of chemical engineering and science in the world, e.g. European Federation of Chemical Engineering (EFCE) in Europe, American Institute of Chemical Engineers (AIChE) in North America, etc. [11].

In the professional societies, educational institutions, students and practitioners have the opportunity to receive numerous teaching materials, as well as to complete on-line and face-to-face programs and obtain certificates in the field of chemical engineering and science.

The Safety and Chemical Engineering Education (SAChE) program, for example, is a cooperative effort between the Center for Chemical Process Safety (CCPS) and engineering schools to provide teaching materials and programs that bring elements of process safety into the education of undergraduate and graduate students studying chemical and biochemical products and processes [12].

One of the benefits of learning in the professional societies is that students expand their knowledge in the fields that often go beyond standard university curricula.

Licensed Professional Engineer

In the USA, UK, and some other countries, licensed Professional Engineer (PE) belongs to a select group of professionals who have made the commitment to achieve excellence in their professional development by initial professional education and experience and by continuing education.

Having a PE after your name signals to employers and clients that you have competence in your field and helps set you apart from your competitors [13-14].

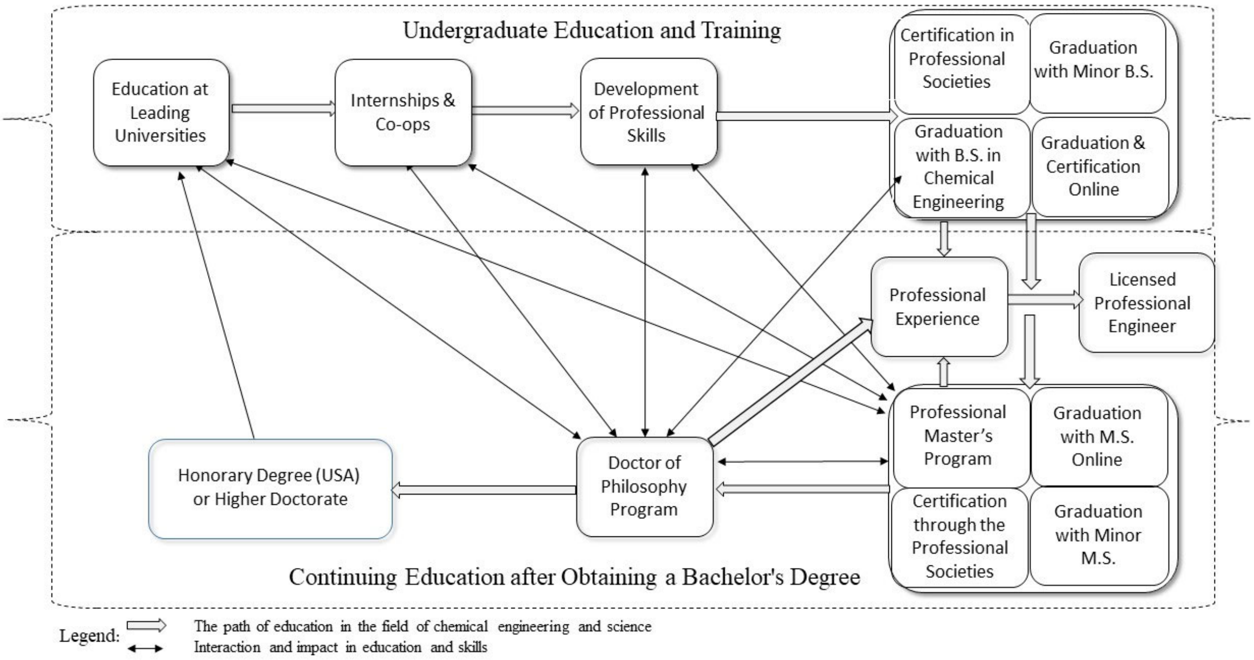

Fig. 1. Continuous improvement in education and training of chemical engineers and researchers.

In order to become a licensed PE, the engineer must hold an engineering degree from an accredited school and pass the fundamentals of engineering exam to earn a training license. After he gains four years of professional experience under the supervision of a licensed engineer, he must then pass the professional engineering exam and earn a full license. After earning the license, the engineer must maintain it by taking continuing education classes and renewing every few years [1].

Some accredited chemical engineering schools offer training programs and classes for students and working professionals to prepare them for the examination for training and professional engineer licenses.

The above path in professional education and training of engineers and scientists in the field of chemical engineering in the United States is reflected in Fig. 1.

It should be noted that such a path of education and training exists in other areas of education in the United States and beyond.

Conclusions

To increase the enrollment of students and meet the growing demand for better education and employment of its graduates, universities must approach their educational process to the business needs.

Continuous professional education and certification of chemical engineering graduates and experienced engineers and scientists at universities and beyond not only increases their employability and earning potential, but also create the conditions and provide the necessary resources to further improve the education and training of students.

Professional knowledge, experience and skills, perseverance, interest in learning and work, and a positive attitude toward colleagues are key elements that contribute to the success of the professional career of chemical engineers and scientists.

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Filtration Drying of Cotton

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Cotton is one of the most valuable raw materials for the production of industrial and food products. Therefore modernization of processing of cotton is extremely important for development of economy of Kazakhstan.According to the state program for Agricultural Development of the Republic of Kazakhstan, in 2017-2021 to 2021 the acreage of cotton in the South Kazakhstan region should increase by 100 thousand tons. Ha, yield – up to 30 cents/ha and production of cotton up to 300 thousand tons./year. Therefore, experimental and theoretical studies of cotton drying are of actual importance.

Keywords: fibrous materials, filtration drying, hydrodynamics, moisture, thermal agent

Introduction

The analysis of the sources of literature [1-3] makes it possible to conclude that there is no complex and systemic approach to the intensification of processes of cotton drying, taking into account the fact that it contains mainly bound moisture, it is a thermolabile material, and The drying process takes place in the second period.

It is known that filtration drying is one of the highly effective methods. The essence of filtration drying is the filtration of thermal agent through a stationary porous layer of wet material, which provides high coefficients of heat and mass. At this, the total waste of energy on the drying process consists of pressure losses in the stationary layer and heating of the heat agent (air) to the desired temperature.

Result of Research and Discussion

The experimental research on the filtration of thermal agent through the stationary layer of cotton in different bulk weight and different heights of a layer represented in the form of functional dependence $\Delta P = f(v_0)$. Generalization of experimental data of the hydrodynamics of filtration of thermal agent through a stationary layer of cotton was conducted in the form of dimensionless complexes. $Eu = f(Re, \Gamma)$, as well as the determined dependence of the hydraulic resistance coefficient of a layer as Reynolds number $\lambda = f(Re)$. The results obtained in dimensionless form provide the possibility to predict energy costs for the creation of pressure differential (in the same hydrodynamic conditions) while designing new drying equipment. Taking into account that the filtration drying has zonal character conducted experimental researches on heat exchange between thermal agent and dry and fibre cotton. The factors of heat transfer for dry fiber cotton determined from heat transfer equation, and wet from the equation of mass-giving. The results of experimental researches were presented as $\alpha = f(v)$, a generalization in the form of functional dependencies $Nu = f(Re, Pr)$ and $Sh = f(Re, Sc)$ .Kinetics filtration Drying of fiber cotton was investigated at different heights of the stationary layer (H = 60 – 160 mm) and temperature of thermal agent T = 318, 333, 353, 373 K, the speed of filtration of thermal agent was 1.0; 1.4; 1.8 and 2.0 m/s. Results Represented in the form of dependence of changes in the in time, as well as changes in drying speed from moisture content. Based on the results of filtration drying, cotton determined the value of an effective coefficient of internal diffusion of moisture in the heat agent.

Conclusion

The dependence of this coefficient on the temperature of thermal agent is established. The results of theoretical and experimental researches are the basis for development of filtration drying technology of cotton and design sizes of filtration drying of cotton.

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THE INNOVATIVE TECHNOLOGIES IN THE CHEMICAL AND FOOD INDUSTRIES

The Estimation of Concentration Polarization Layer Resistance During Salt Solutions Reverse Osmosis

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Abstract* – *The experimental determination of the concentration polarization layer during salt solutions reverse osmosis. It was defined that assumption about linear dependence of concentration polarization layer resistance from applied pressure is reasonable not only for ultrafiltration but also for reverse osmosis.

Keywords – membrane, reverse osmosis, concetration polarization, resistance, pressure, mass tramsfer.

Introduction

The concentration polarization phenomenon is one of the most significant problems in applications of pressure-driven membrane processes, which often lead to bigger problems such as fouling formation and irreversible drop of membrane units productivity. Taking into account these phenomena, according to [1] the transmembrane flux could be described by that equation:

$$J = \frac{\Delta p - \Delta \pi}{\mu \cdot \left(R_m + R_{cp} + R_f\right)} \qquad (1)$$

The methods for determination of membrane resistance (Rm) and fouling resistance (Rf) are described in works [1] and [2] but reliable dependencies for determination of concentration polarization layer (Rcp) was not found in the literature.

The most comprehensive research about the concentration polarization layer resistance was done in work [3]. In that work, the assumption about linear dependence between concentration polarization and applied pressure has been done. The proportional coefficient was determinated from experimental data approximation using the dependence obtained from transformation of Eq. (1):

$$\frac{1}{J} = \mu \cdot \left(R_m + R_f\right) \frac{1}{\Delta p} + \mu \cdot \psi \qquad (2)$$

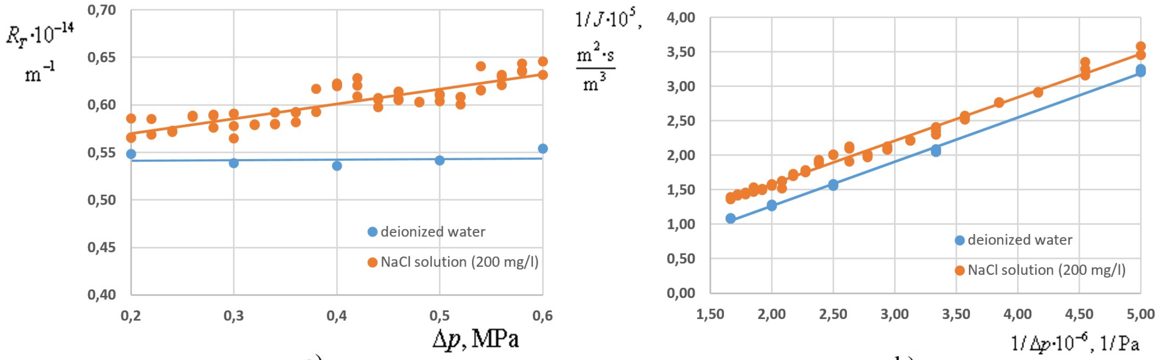
However, the physical sense of proportional coefficient and extends of usability of that technique have been not described in work [3]. In our recent work [4] the attempt of determination of concentration polarization layer resistance and validate of the possibility of using such technique for reverse osmosis have been done, but the obtained results were not allowed to confirm mentioned assumption. However, the feasible reason for this problem was a big step of applied pressure variation. The purpose of present work is the evaluation of the concentration polarization layer and examination the assumption about linear dependence between the concentration polarization layer and applied pressure.

Materials and Methods

The research was carried out on the experimental set-up of crossflow reverse osmosis with new (without fouling) membrane modules TFC-75. The NaCl solutions and deionized water were used as test solutions. The step of applied pressure variation was 0.02 MPa whereas in previous work it was 0.1 MPa [4]. The range of applied pressure variations was 0.2–0.6 MPa. The experiments were carried out under the temperature of the environment.

Results and Dicussions

The results of experimental research are shown on Fig. 1.



a) b)

Fig. 1. The results of experiments: a) dependence of total resistance to mass transfer thorough the membrane from applied pressure b) dependence $1/J = f(1/\Delta p)$

From the dependence of total resistance from applied pressure (Fig. 1a) it could be seen that when deionized water is used as test solution the total resistance did not change with applied pressure with confirms the conclusions about absence change in membrane productivity due to compression obtained in previous work [4]. When the salt solutions were separated by reverse osmosis, the increasing of total resistance with applied pressure was observed which are close to linear. In considered conditions, the total resistance was the sum of membrane resistance and concentration polarization layer resistance, therefore, concentration polarization layer resistance also increases linearly. The reason of scattering of points is the deviation from isothermal condition during experiments. However, even in such conditions, the dependence of resistance from applied pressure could be approximated by a linear equation with the correlation coefficient of 0.85, which gives evidence that mentioned assumption is reasonable. Moreover, from Fig 1b, it could be seen that dependence $1/J=f(1/\Delta p)$ can be approximated by linear equation (correlation coefficient is 0.95) which confirmed that technique proposed in [3] is also suitable for reverse osmosis.

Conclusion

The assumption about linear dependence between concentration polarization layer resistance and the applied pressure is reasonable. The technique for data analysis of membrane productivity proposed in work [3] for ultrafiltration also can be used for reverse osmosis.

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The Hydraulic Resistance in the Small-Scale Pillow-Plate Heat Exchangers

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***Abstract* – The Pillow-Plate Heat Exchangers (PPHEs) are rated as innovative type of heat transfer equipment. The present paper gives the information about the research made in Paderborn University aimed to investigate the heat transfer and pressure drop in the channels of the small-scale PPHE.**

Keywords – heat exchangers, pillow plates, heat transfer, heat exchanger design, hydraulic resistance.

Abstract

The so-called Pillow-Plate Heat Exchangers (PPHEs) are innovative type of heat exchange equipment. They have space-effective, light and pressure-resistant construction and show intensified heat transfer and low pressure loss on the product media side [1]. PPHEs are produced by spot-welding of two steel sheets, followed by hydro-forming to obtain channels for heat carrier movement. In case of condensers, the cooling medium flows on the inner side forming a cooling channel, whereas the vapour flows on the outer side (between cooling channels). The edges are fully seam-welded. The schematic of a pillow plate with its main geometrical parameters are presented in Fig. 1. Pillow-plate surfaces of PPHEs ensure the turbulent movement of heat carriers inside the channels formed by the plates. The particular waviness of the pillow-plate channels promotes lateral mixing and beneficial turbulence, which results in a good thermo-hydraulic performance. The manufacturing technology of PPHEs is extremely flexible, and the diversity of the resulting geometries is immense. The application area of PPHEs is broad and expanding. In contrast to conventional equipment, however, no reliable design methods for compact PPHEs are available in the open literature [2].

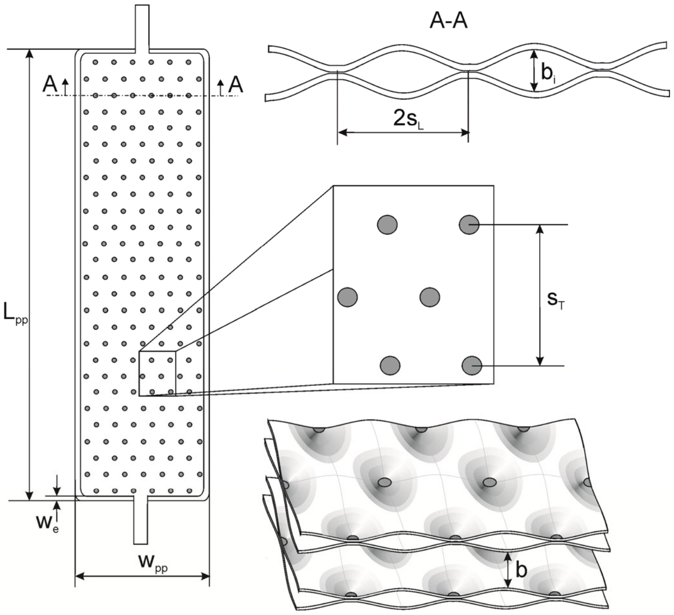

Fig.1. The schematic of pillow plate with specification of its main geometric parameters.

The reliable design of PPHEs includes the identification of the geometrical parameters (gap width, height and length of the plates) and estimation of heat transfer and hydraulic parameters of the unit and is mostly influenced by the geometry of the heat transfer channels, which determine the heat transfer and hydraulic parameters of the unit. The standard pillow plates are assembled together in one unit, what enables to vary the distance between them, and consequently adjust the hydraulic resistance and heat transfer process in the outer channels between welded pillow plates (external or E-channel). The geometry of inner-plate channel (inner or I-channel) determines the whole performance of the PPHE. The geometries of I-channels for the investigated small-scale PPHE are presented in [3]. The description of the experimental set-up for investigation of hydraulic resistance in small-scale PPHE is published in [3]. The empirical equations for calculation of friction factors in the I-channel, which has smaller cross-section area, ζ1 was derived from the experimental data based on the form of equation proposed by Churchill [4] for straight tubes and has the following form:

$$\zeta = 8\cdot\left[\left(\frac{12+p2}{Re}\right)^{12}+\frac{1}{(A+B)^{\frac{3}{2}}}\right]^{\frac{1}{12}} \quad A=\left[p4\cdot ln\left(\frac{p5}{\left(\frac{7\cdot p3}{Re}\right)^{0.9}+0.27\cdot 10^{-5}}\right)\right]^{16} \quad B=\left(\frac{37530\cdot p1}{Re}\right)^{16} \quad (1)$$

where p1 to p5 are parameters defined by the channel form and for the investigated small-scale PPHE are equal: p1=136.321; p2=7.387; p3=0.382; p4=0.515; p5=4.622.

The friction factor in E-channel ζ2 was obtained based on the experimental data, and has the following form:

$$\zeta = 0.7155\cdot Re^{-0.361} \qquad (2)$$

Values calculated according to Eqs. (1), (2) differ from experimental data by less than □10 % and are valid in the range of Reynolds numbers between 2,000 and 20,000.

Conclusion

In this work, the experimental data for hydraulic resistance in small-scale PPHE were obtained. The correlations for friction factor in PPHEs inner and outer channel were worked out, with a deviation from experimental results within 10 %. They are reliable for the Reynolds numbers varying between 2000 and 20000.

Acknowledgments

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Prospects for Implementing the Principles of Innovation Policy in Ukraine

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***Abstract* – Innovation is an integral part of economic activity and scientific, technical and industrial development. To implement innovation, it is necessary to form an innovative policy of the state. An integral part of stimulating innovation is the level of investment in the relevant sectors of the economy.**

Keywords – innovations, innovative technologies, innovation policy.

Introduction

Since the late 20th century, the close combination of the scientific and industrial and economic activities has led to the emergence of innovations with signs of systemicity that required the regulation of systemic innovations at the state level. The aim of regulation should be to support the environment to stimulate the creation, dissemination and implementation of innovations in the industry. In developed countries, at the national level, there are specialized institutions for stimulating innovation, which is intended to strengthen the scientific and technical base and enhance the competitiveness of the national economy.

Principles of Innovation Policy

According to J. Schumpeter, the definition of innovation includes the use of new technology, technological processes or new market supply of production; introduction of products with new properties; use of new raw materials; changes in the organization of production and its logistical support; the emergence of new markets. In turn, innovations can be classified according to the following features: for the subject-content structure; by appointment; by factors of social production; by the level of development and distribution; for novelty; in the areas of development and application; originally; on the innovative potential; by stages of life cycle and duration. From the above, innovation is now an integral part of any kind of activity in modern society, but first and foremost, innovation must be an integral part of the economic activity and the scientific and technical, and, accordingly, industrial development of the country, and formulate an innovative policy.

In accordance with national priorities defined at the state level, a wide range of tools and methods are used to stimulate innovation activity. Such methods include the correction of patent and tax legislation; control over technology spread; introduction of a system of contractual relations; application of methods of supporting inter-organizational cooperation; stimulating innovation in small business, etc. [1]. An integral part of stimulating innovation is the level of investment in economic activity. The breakdown of the level of investment in perspective industries of the Ukrainian economy according to the data of the State Statistics Service of Ukraine in the period from 2010 to 2017 is shown in Table 1.

The growth of investments into the Ukrainian economy after the expected fall in 2013-2014 is traced. Along with the growth of the total volume of capital investments into the Ukrainian economy, the volume of investments in hryvnias increased in comparison with 2010: in the industry by 2,6 times; in agriculture 5.9 times; in the IT sphere 5.9 times. When calculating the volume of investments in dollar equivalent, considering the inflation rate, the total volume of investments in the Ukrainian economy decreased by 1.35 times. The growth of investments in the dollar equivalent is observed only in agriculture - an increase of 1,75 times and in the IT sphere - an increase of 1,76 times. But the main thing is that there is a positive dynamic, which testifies to the gradual recovery of the economy.

Table 1

Capital investment by types of economic activity for 2010-2017 years, millions of UAH

	2010	2011	2012	2013	2014	2015	2016	2017
Industry	55384.4	78725.8	91598.4	97574.1	86242	87656	117753.6	143300
Agriculture	10817.7	16140.9	18564.2	18175	18388.1	29309.7	49660	63400.7
IT sphere	347.5	580.2	621.2	634.5	670.3	1134.3	2124.9	2050.6
Scientific research and development	549.7	717.9	548.8	599.2	375.4	518.2	758.3	1110.2
Education	1818.4	2090.7	1463.5	1030.5	820.9	1540.1	2257.3	3492.5
Total (mln. UAH)	180575.5	241286	273256	249873.4	219419.9	273116.4	359216.1	448461.5

In 2017, there was a rather low level of investment in the perspective directions of development of the Ukrainian economy, namely, in agriculture - 14.14% of total investments, and in the IT sphere - 0.46%! As of 2017, we see an inappropriate investment in key industries that should ensure the global growth of innovation in the national economy: investment in research is 0.25%; Investing in education is only 0.78%. The highest level of investment fell in the industry. The chemical industry together with the metallurgical industry is the key areas of the entire Ukrainian industry. One of the promising directions for introducing innovations in the chemical industry may be the use of biological resources in chemical production [2]. The transition to domestic renewable resources will reduce the dependence of the Ukrainian economy on imported raw materials - oil and gas. This direction of development of the chemical industry will also improve the situation with the ecological safety of chemical production, increase the safety of chemical products in general, both in its use and at the end of the life cycle [3].

Conclusion

The development and implementation of innovations should be the key to the development of the Ukrainian economy because only innovations can provide Ukraine with a proper place in the global economy. Otherwise, we expect an increase in the lagging behind the leading countries and the final descent into the group of third world countries. It is necessary to develop state programs of stimulating innovations considering the best world models. An important component is to promote the attraction of both domestic and foreign investments. This requires changes in legislation, the tax system and the increase of public investment in education and research. One of the promising directions is also the use of biotechnology in the chemical industry, which will enable the practical implementation of the theoretical foundations of macroeconomic regulation of environmentally-directed innovation development.

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The Investigation of Hydrogels Composite Filling by Gelatin

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Abstract* – *The paper describes the synthesis and investigation of the properties of acrylamide and acrylic acid hydrogel composites with a crosslinking agent with gelatin, unmodified or modified peroxide oligomer, which can be use to create cosmetic products. The method of synthesis of hydrogel composites described and their physical, chemical, thermomechanical properties and graphic representation of these regularities presented. To do this, a series of samples with different ratios of starting substances synthesized and the dependence of their properties on the structure is established.

Keywords – polymer composite, hydrogels, gelatin, swelling.

Introduction

Hydrogels are one of the perspective classes of polymer systems that embrace numerous biomedical and pharmaceutical applications. Hydrogels have become very popular due to its unique properties such as high water content, softness, elasticity and biocompatibility. Natural and synthetic hydrophilic polymers can be physically or chemically crosslinked to obtain hydrogels. Their resemblance to living tissue opens up many possibilities for applications in biomedical fields. Hydrogels are widely used for various biomedical applications − tissue engineering, molecular imprinting, monopoles as dressings, drug delivery and other.

The aim of the present research is obtaining hydrogel composites filled with gelatin for cosmetic application.

Experimental

By graft-polymerization of hydrophilic functional monomers in an aqueous medium obtained spatially, crosslinked polymer hydrogels filled with gelatin (Gel). For this purpose, a process conducted in water solution of monomers (acrylamide (AкAм), acrylic acid (AcA)) in presence gelatin and modified gelatin peroxide modifier. In the case of using the modified gelatin of the initiation of polymerization occurred due to the decomposition of peroxide groups immobilized to the surface of the gelatin molecules. The paper presents the evolution of swelling of the gelatin composites with grafted macromolecules of polyacrylamide and polyacrylic acid and different ratios of filler and copolymers.

The degree of swelling (D.S.) was determine by equation is Eq. 1:

$$\alpha = \frac{m - m_0}{m} * 100 \qquad (1)$$

α – the degree of swelling %mas, m – weight of swollen composite, g; m0 – the weight of the dry composite, g.

Taking into account, the presented results are noticeable sharp increase in the maximum values of swelling in comparison with the samples of grafted polyacrylamide. This is probably due to the formation of an additional stitched mesh between grafted copolymer through centers of interaction between functional groups of macromolecules –NH2 and –COOH. Composites filled with modified gelatin show mass storage, and therefore shape, with long periods in a water environment. This suggests that the modified gelatin has the satisfactory properties of the crosslinked agent.

Figure 1 demonstrated the kinetics of swelling of polymer hydrogel composites based on unmodified gelatin, acrylamide and acrylic acid, which differ in the content of gelatin.

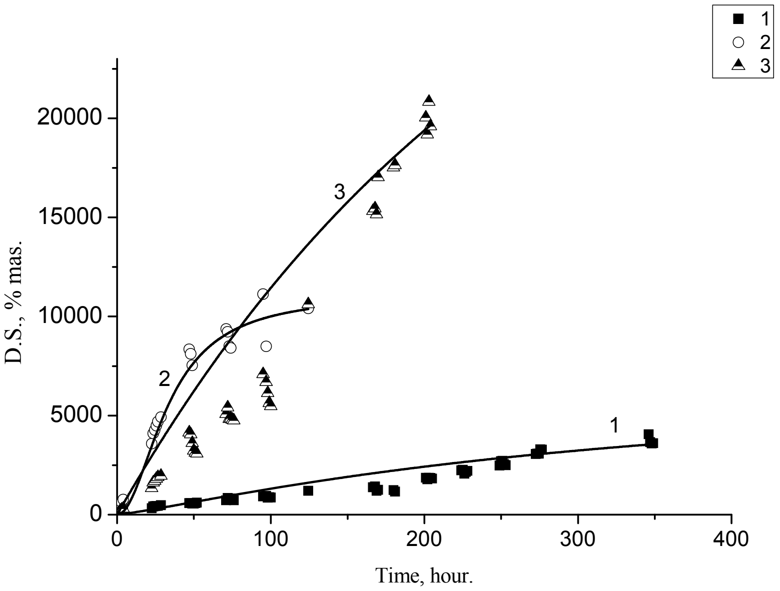

Fig.1. The kinetics of swelling of hydrogel composites.
The composition of the copolymer 1: %mas: Gel.=20, AкAм=40, AcA=40;
The composition of the copolymer 2, % mas: Gel.=10, AкAм=45, AcA=45;
The composition of the copolymer 3, % mas: Gel.= 5, AкAм= 47,5, AcA=47,5;

The results show that the best sorption properties of the sample has a content of 5% wt. gelatin. However, the increase of content of gelatin results in the best mechanical durability and possibility of the protracted storage.

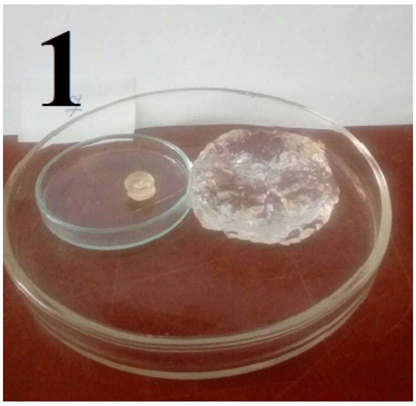

Fig.2. Photo hydrogel composites before and after swelling

Conclusion

As a result of conducted research, the obtained hydrogel composites with various composition and ratio of components: gelatin (unmodified and modified by the peroxide oligomer of VEP-MA), acrylamide, acrylic acid and starch. The kinetics of swelling of hydrogel composites and determined the rate constants of swelling. The change of sizes of relative change of sizes of the obtained hydrogel composites is calculated and presented.

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Perspectives of Use a New Generation Granulated Organic-Mineral Fertilizers

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***Abstract* – The main problems of preservation and increase of soil fertility with the use of multilayer granular organic-mineral fertilizers, which contains humic organic compounds, deoxidizing impurities and mineral components are considered. The urgency of creation of new resource-saving technologies for the production granular organic-mineral fertilizers from waste of chemical, food and agrarian productions are determined.**

Keywords – soil fertility, organic-mineral fertilizers, resource conservation, granule.

Introduction

The strategy of sustainable development of Ukraine as a state, a significant part of the export, which is the export of agricultural products, includes the development of the agro-industrial complex, strengthening of competitiveness on the market, increase of markets for production, preservation of natural resources and protection of the environment.

Ukraine belongs to one of the leading countries in the production and sale of agricultural products, as of 2018, the share of exported vegetable agricultural products is 20,9 % to the total volume of foreign trade of Ukraine, of which 15,3 % is the export of grain crops [1]. The diagram of the main commodity exported products is shown in Fig. 1.

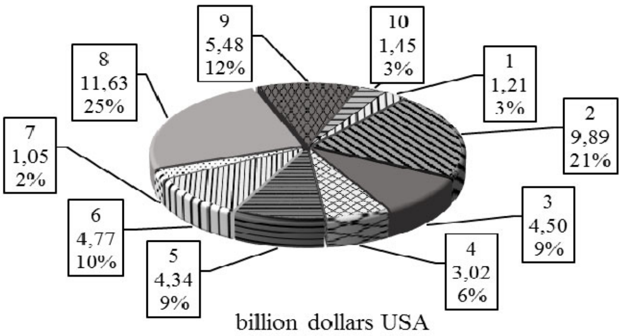

Fig.1. Commodity structure of Ukraine's exports in 2018

1 – livestock products; 2 – plant products; 3 – fats and oils; 4 – finished food products; 5 – mineral products; 6 – products of the chemical and allied industry; 7 – textile materials, leather and clothing; 8 – base metals; 9 – machines, equipment and machinery; 10 – other

Due to the fact that gross collections of agricultural plant products depend on soil fertility, increasing and maintaining the fertility of all available soils is one of the main strategies for economic development.

In order to meet the food and export needs in Ukraine, the agricultural area has been increased, which is approximately 53,9 % of the total area of the territory [2]. Increase in soil tillage leads to deterioration of ecological balance. Therefore, in order to preserve ecological balance, it is necessary to reduce the amount of arable land to 33% of the total area of the territory, that is, to reduce the area of arable land by 24 % or to withdraw from land use 14 million hectares of agricultural land [3].

Recently soil fertility has been rapidly decreasing because of irrational land use, soil erosion, pesticide and herbicides contamination, mineral fertilizer residues, adverse weather conditions and soil compaction when cultivated with agricultural machinery. Of the total area of about 12,9 million hectares of arable land destroyed by water and wind erosion. Annual loss of humus from soil is 1,08 tons per hectare in Ukraine in general [4]. Also very significant impact on the reduction of soil fertility have reducing the balance of nutrients, decalcification and physical degradation.

Another important scientific and technical problem is the creation of non-waste land use and reuse of waste from the food, chemical and agrarian industries as raw materials for the production of fertilizers.

Main Part

Agrarians make a large amount of mineral fertilizers every year in order to maintain a stable harvest. In 2016 into the soil were introduced over 1724,4 thousand tons of mineral fertilizers, which is irrational use of mineral resources [4]. Excessive use of mineral fertilizers leads to an increase in the concentration of mineral salts in the soil, resulting in the destruction of the structure of the soil, in the vegetables accumulate harmful to health of nitrates and phosphates, erosion of water-soluble components of fertilizers and their entry into groundwater and reservoirs [3].

Application of mineral fertilizers has a number of shortcomings, but the complete refusal of their use is also undesirable, as the termination of their application will lead to a decrease in plant yield due to lack of plants essential for the normal development and functioning of such important substances as nitrogen, phosphorus, and potassium. To solve this problem is the use of complex granular organic-mineral fertilizers with a given composition of components in accordance with agro-climatic conditions of cultivation.

The development of agrarian industry is impossible without the improvement of available fertilizers and technology of their production. The relevance of using a new-generation fertilizers, which includes controlled and slow release fertilizers is increasing. The main reasons for this are their high efficiency compared to conventional fertilizers. Fertilizers of slow release and controlled action are fertilizers that contain plant nutrients in a form that allows them to slow down their release and absorption by the plant after application, or prolong the period of their availability in the soil.

To create these fertilizers it is necessary to determine the beneficial effect of each component, placement and concentration in the granule. It is also necessary to create technological bases for the production of fertilizers with the use of various wastes of the food, chemical and agrarian industries. Organic raw materials for the production of these types of fertilizers may be peat, brown coal, hydrolyzed lignin and other organic residues and waste from agrarian and food industries [3].

The choice of components to the granular OMF of prolonged or controlled action depends on many factors. The most important physical and chemical parameters are adhesion, aggregate state and solubility of components on which the choice of equipment and process depend on. The most important agro-climatic parameters include the regime of moisture and soil condition. For acid soils, it is possible to add to the granular fertilizer a deoxidizing component, such as lime and calcium carbonate. In conditions of arid climate and uneven rain regime in the form of integrated granular fertilizers, it is possible to add components with certain physical-chemical properties. The list of proposed useful components are shown in table 1.

Table 1

List of proposed components and their functions in the fertilizers

№	A useful ingredient in fertilizer	Component function
1	Ammonium sulfate, nitrate, ammonium phosphate, urea (carbamide), potassium sulfate, potassium chloride	Nutrition of plants with mineral compounds N, P, K.
2	Humic components from brown coal and peat, lignin, compost (bio humus), disinfected and treated waste from livestock and poultry, bone meal.	Restoration of the level of humus in the soil, creating a nutrient medium for the propagation of useful microorganisms.
3	Calcium carbonate, lime	Neutralization of acid soils.
4	Gypsum.	Neutralization of alkaline soils..
5	Bentonite clay, zeolite, perlite.	Preservation of fertilizers from washing, moisture sorption and its content in the granule, prevention of explosive properties of fertilizers.
6	Sulfur, phosphogypsum, phosphorous flour, peat, fatty acid salts, calcium and magnesium phosphates, magnesium oxide, polymers (polyethylene, ethylene vinyl acetate, polyesters, carbamide formaldehyde resins and others).	The containment (encapsulation) components inside the granule and their controlled release, depending on the soil conditions, temperature and water content.

It is also possible to add to the granules potassium salts, chalk, phosphorous flour, phosphogypsum and many other useful components, which are usually introduced separately and will allow the plant to provide all the necessary nutrients and trace elements.

Conclusion

The main advantages of complex granular organic-mineral fertilizers are the high degree of assimilation of useful components and slow release of useful components in the soil, which is provided by the multilayer structure of granule. Application of organic-mineral fertilizers of this type allows to restore soil fertility and to dispose of it from the chemical, food and agrarian industries. In the production of these fertilizers the most important stage of production is the process of granulation, so the study of this process is an important scientific and technical task.

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Synthesis of Catalysts Based on Magnetic Particles $CoFe_2O_4$

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***Abstract* – Magnetically sensitive catalysts of the core-shell type based on stabilized particles of cobalt ferrite and copper oxide by the sol-gel method were obtained. A multistage manufacturing technology of the composite $CoFe_2O_4/SiO_2/CuO$ is proposed. Qualitative and quantitative microanalysis of the obtained composite were carried out and its catalytic action was investigated in the process of the initiated oxidation of cumene. The resulting nanocatalyst is promising for use in the oxidation processes of hydrocarbons.**

Keywords – heterogeneous catalysis, sol-gel synthesis, core-shell type catalysts, TEOS, initiated oxidation of cumene.

Introduction

The creation of catalytic systems based on a magnetic core stabilized by silicon oxide and active centers on the surface of the particles is a topical issue both for chemical synthesis and for ecology and restoration of water resources. Such porous catalysts with magnetic properties (core-shell type) have several advantages: good adsorption capacity, the possibility of magnetic separation and recirculation at room temperature and heat resistance.

Results and Discussion

The developed method for the synthesis of nanostructured magnetically sensitive catalysts of the core-shell type $CoFe_2O_4/SiO_2/CuO$ includes three stages. At the first stage, the synthesis of cobalt ferrite particles, which form a magnetically sensitive core. The second one is the application of an intermediate layer of silica by sol-gel method. The third stage is the formation of an outer layer of copper oxide, which exhibits catalytic properties.

The obtaining of $CoFe_2O_4$ nanoparticles was carried out by coprecipitation from a solution of iron (III) and cobalt (II) nitrates (at a molar ratio of 2:1) by adding ammonium hydroxide in the presence of surfactant under intense mixing at 80 °C.

The reaction of synthesis can be represented by the following equation:
$2\ Fe(NO_3)_3 + Co(NO_3)_2 + 8\ NH_4OH \rightarrow Co(OH)_2 + Fe(OH)_3 + 8\ NH_4NO_3 + 4\ H_2O$

After evaporation and calcination of the obtained hydroxides at a temperature of 300 °C, porous particles of cobalt ferrite with a developed specific surface and pronounced magnetic properties are formed (Fig. 1).

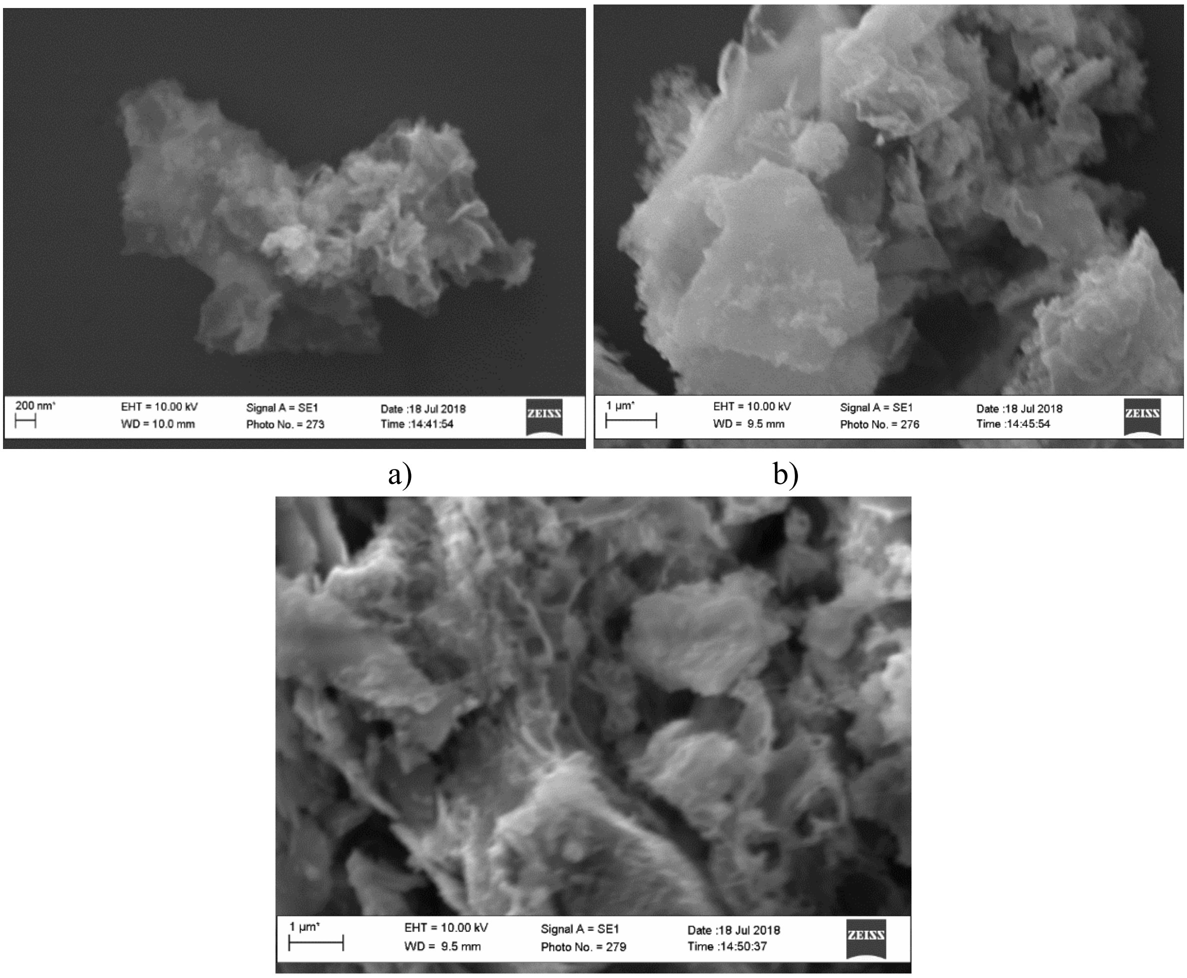
Fig. 1. Photo of $CoFe_2O_4$ particles after annealing

The application of an intermediate layer of SiO_2 is aimed at stabilizing $CoFe_2O_4$ particles and preventing their aggregation. In addition, the presence in the surface layer of the material silanol groups of silicon dioxide enables the formation of chemical bonds with modifiers at the next steps.

The precipitation of SiO_2 was carried out by the method of sol-gel synthesis using tetraethoxysilane (TEOS) as a precursor of silicon dioxide. The amount of tetraethoxysilane was calculated from the molar ratio $CoFe_2O_4$:SiO_2 = 2,5:1. To particles $CoFe_2O_4$ dispersed in water, tetraethoxysilane was injected in the form of an alcoholic solution. The precipitation was carried out using ammonium hydroxide with vigorous stirring at 40°C for 4 hours. The obtained precipitate was washed and left in water in dispersed form.

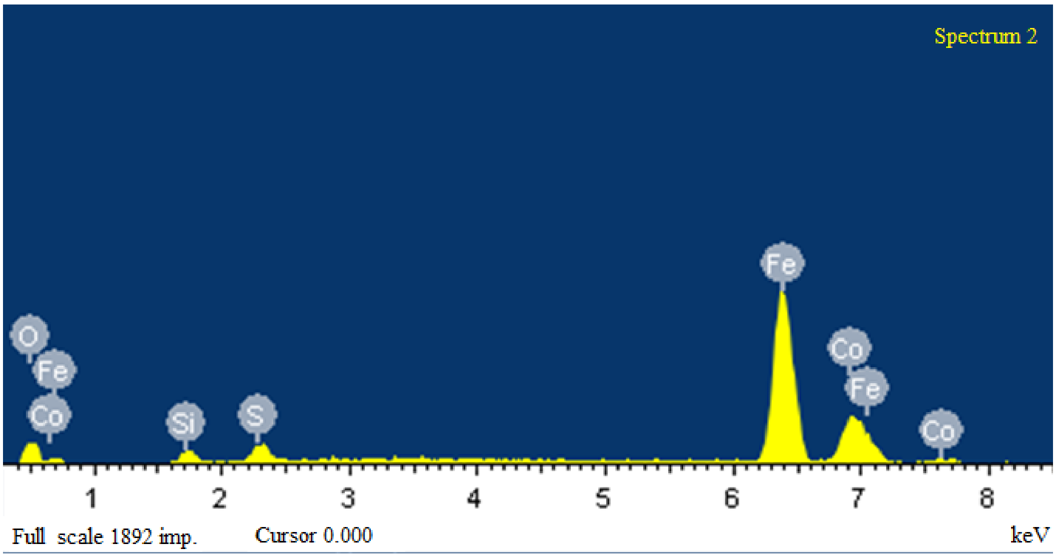
To form the catalytic layer, a solution of copper acetate was added to the reactor at the molar ratio $CoFe_2O_4$:CuO = 1:1. The precipitation of $Cu(OH)_2$ on the surface of the formed $CoFe_2O_4/SiO_2$ particles was carried out by adding an equimolar amount of NaOH. After washing to pH = 7 and drying at 100°C for 24 hours, the obtained precipitate was calcined at 300°C for 1 hour. With this technology, the formation of copper oxide on the surface of the particles, which is bonded to the particle by chemical bond.

The study of the morphology of the obtained composites showed that the particles of cobalt ferrite have a finely dispersed structure of micron sizes (Fig. 2a). The analysis of the obtained spectrums indicates that, in addition to cobalt ferrite, part of the atoms of the ferrum exists in the form of the mineral of maghemite γ-Fe_2O_3 (Fig. 2b). When applied to the surface of cobalt ferrite particles of a dense layer of SiO_2 (Fig. 2c) and a layer of copper oxide (Fig. 2d), an increase in the size of particles with the preservation of the developed surface is observed.



a) b)

c)



Element	Gravimetric %	Nuclear %
O K	7.27	21.00
Si K	2.10	3.46
S K	2.19	3.16
Fe K	69.09	57.20
Co K	19.35	15.18
Total	100.00	

d)

Fig. 2. SEM photographs of samples of synthesized composites: $CoFe_2O_4$ (a), $CoFe_2O_4/SiO_2$ (b), $CoFe_2O_4/SiO_2/CuO$ (c) and spectrogram of the sample composition $CoFe_2O_4$ (d)

The catalytic action of the obtained composite was determined in the process of initiated oxidation of cumene by molecular oxygen. The use of the composite $CoFe_2O_4/SiO_2/CuO$ as a catalyst in the process of cumene oxidation allows to increase in the process rate by an order, depending on the amount of the used catalyst (Fig. 3).

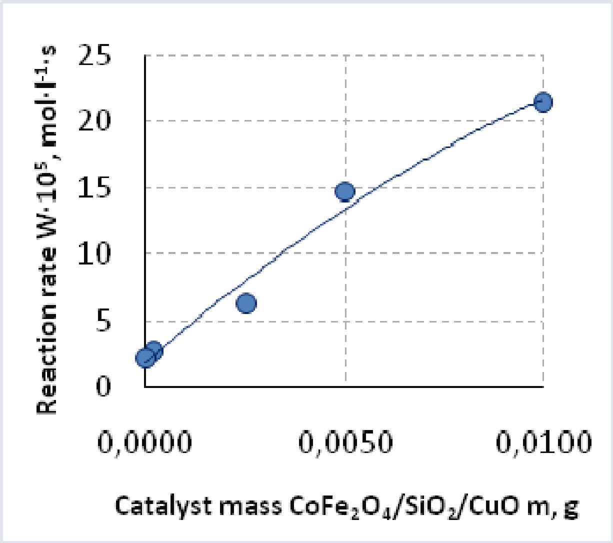


Fig. 3. Dependence of the reaction rate of initiated cumene oxidation on the amount of catalyst $CoFe_2O_4/SiO_2/CuO$

In addition, the obtained catalyst demonstrated the ability to work for several cycles without regeneration and without loss of catalytic activity.

Conclusion

The research results showed that the composite $CoFe_2O_4/SiO_2/CuO$, made a according to the proposed technology, can serve as a catalyst for the process of initiated cumene oxidation.

Intensification of the Mass Transfer Processes in the System "Solid-Liquid" by Use of Inert Gas

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Abstract* – *The methods of intensification of mass transfer processes in the solid - liquid system are considered. The classification of methods and conditions of action for this system is given. Attention is paid to non-stationary phenomena and analogy to heat transfer processes. An overview of the methods used for the intensification of chemical processes is given.

Keywords – mass transfer, heat transfer, intensification, dissolution.

In the chemical industry various methods of intensification of technological processes are used. These methods include mechanical mixing, fluid circulation, inertial and centrifugal regimes, overlaying of stationary force fields, mechanical and physical vibration overlays, and others. The above methods show intensifying action, increasing the rate of flow of solids and the surface of interaction, updating the interaction surface. Significantly intensifying action for mass transfer in the solid-body system is a gas phase that generates various effects in the two-phase system, which facilitate the acceleration of mass transfer. Below we will present methods for using the gas phase to intensify technological processes, their impact on mass transfer and gas generation methods. The main role of the gas phase is in its influence on hydrodynamics, which is the main driving force of mass transfer. The gas phase causes the fluid to move or accelerates it. The task of researchers is determftion or evaluation of this speed.

1. Inert gas delivery to the system "solid-liquid":

Continuous process of motion of a gas-liquid emulsion in the apparatus: fluid turbulization; increase in speed due to the presence of gas; reduction of the thickness of the boundary diffusion layer (BDL), which increases the coefficient of mass transfer; partial shielding of the surface and installation of non-stationary phenomena is possible.

Dissolution in periodic apparatus: occurrence of turbulent fluid fluctuations; evaluation of the pulsating velocity of the process; non-stationary dissolution process; determination of the characteristic linear dimension of the pulsation motion.

2. The emergence of the vapor phase on the surface of solids: turbulence of the BDL due to bubble vapors that arise and grow on the surface; non-stationary process; the movement of liquid in the capillaries of the solid phase and the replacement of molecular diffusion by turbulence; partial concentration of the solution.

3. Isolation of gas phase in diffusively controlled processes: dependence of the coefficient of mass transfer on the concentration of the reagent; analogy with heat exchange with boiling liquids; influence of mechanical and pneumatic mixing on mass transfer; thermal aspects of these processes.

4. Cavitational processes with the formation of steam-gas mixtures: the occurrence of ions and radicals; intensification of diffusion processes; intensification of kinetic-dominated chemical processes; effect on microorganisms.

5. Vibration, microwaves, ultrasound and other physical methods of intensification.

6. Joint action of gas phase with other methods of intensification.

Synthesis of Acrylic Acid and its Esters with Se-Containing Catalysts

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***Abstract* – Se-containing catalysts of organic and inorganic nature were explored for the synthesis of acrylic acid and its esters in different solvents. Newly synthesized Se-containing microgel catalyst shown the best catalytic performance. With microgel catalyst different acrylate monomers can be produced with high yield simply by varying solvent nature.**

Keywords – acrolein, acrylic acid, methyl acrylate, ethyl acrylate, butyl acrylate, Se-microgel catalysts.

Introduction

Acrylic acid and acrylate esters are widely used in industrial purposes for textile, adsorbent polymer, paints, adhesives manufacture [1]. Main method to produce acrylic acid is 2 step synthesis, that include propylene oxidation to acrolein with further acrolein oxidation to acrylic acid [2]. Acrylic acid can be used without further treatment or esterified to acrylate esters. Another method to produce acrylate esters is one-step oxidative esterification of acrolein [3]. Previously reported results [3, 4] shown, that up to 85 % of methyl acrylate yield can be reached by this method. But to achieve such result, either reaction temperature has to be high (250 ºC) and catalyst, that contain hazardous heavy metals, has to be used [4] or reaction can be performed at moderate temperature (25 ºC) but reaction has to last 40 h [3].

To improve process of acrolein oxidation to acrylic acid or oxidative esterification to acrylate esters, reaction should be performed under mild conditions, during reasonable time, with minimum wastes and with high yield of product. Selenium catalysts shown to be effective in oxidation processes [5], and together with hydrogen peroxide as oxidant can provide good results under mild and green conditions [6]. For this purposes, we studied process of acrolein oxidation with hydrogen peroxide and selenium catalysts of organic and inorganic nature.

Results and Discussion

In term to study the effect of catalyst nature on acrolein oxidation and oxidative esterification, reactions were performed at 50 ºC with catalysts 0.0044 mmol/ml concentration, reaction time – 8 h, oxidant – hydrogen peroxide. Methanol, ethanol, butanol and dioxane were used as solvents. H_2SeO_3, diphenyl diselenide (DPDS), diselenide crosslinker (X-linker, Fig. 1a), Se-modified microgel (Fig. 1b) were used as Se-containing catalysts.

Se-modified microgel consists of diselenide crosslinker, incorporated into poly(*N*-vinylcaprolactam) microgels together with a permanent *N,N′*-methylenebis(acrylamide) crosslinker. Microgel, as polymer colloid with open porous structure, surface activity and solvent resistance, can provide unique chemical functionality and catalytic activity of modified microgel.

Catalytic performance of Se-containing catalysts was evaluated by the yields of methyl acrylate and acrylic acid for the reaction performed in methanol (Fig. 2). All tested catalysts proved to be catalytically active in oxidative esterification of acrolein and allowed to reach up to 90% total yield of reaction. Regardless the catalyst, methyl acrylate yield was much higher than acrylic acid. This results are in good correlation with results in work [3], where authors explain higher yield of ester due to easier formation of intermediate compound in ester synthesis than in carboxylic acid synthesis. Diphenyl diselenide, X-linker and H_2SeO_3 shown similar results. Se-modified microgel shown the highest yield of reaction – 89 %.

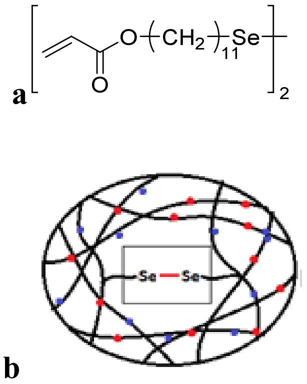

Fig. 1. a – Diselenide crosslinker; b – Se-modified microgel

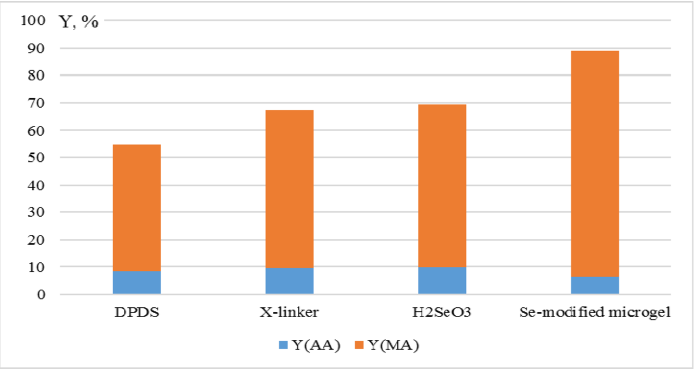

Fig.2. Effect of catalyst nature on acrylic acid (AA) and methyl acrylate (MA) yield

To study the effect of solvent nature on the synthesis of acrylic acid and acrylate esters, Se-modified microgel was used as the most effective catalyst. In methanol medium, ester yield and ester:acid ratio was the highest – 83 % and 12:1 respectively. With increase of hydrocarbon chain in alcohol molecule (C_2H_5-OH and C_4H_9-OH) ester:acid ratio decreases, but ester yield is still higher than acid. In dioxane medium only acrylic acid was formed with 79 % yield.

Conclusion

Acrylic acid and acrylate esters can be easily synthesised in one step reaction from acrolein with yield up to 79 % and 83 % respectively with Se-modified microgel catalyst. Products of the reaction and their ratio can me modified by chosen solvent.

Acknowledgments

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Technological Aspects of the Production of Functionalized Hydrocarbon Oligomers

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Abstract* – The paper is devoted to the oligomerization process of unsaturated hydrocarbons fractions are contained in hydrocarbon fractions of liquid products of pyrolysis in the presence of the peroxides initiator with high integral procedural decomposition temperature. Hudrocarbon fraction contains valuable unsaturated compounds, which have high reactivity and are easily subjected to oligomerization. The proposed technological schemes are based on the developed block schemes for the production of functionalized hydrocarbon oligomers on the basis of existing technologies.

Keywords – oligomerization, hydrocarbon fraction, initiator, monomer, oligomer.

Introduction

Hydrocarbon oligomers were catalyzed by oligomerization, they were effectively used as plasticizing impurities for natural and synthetic rubbers due to the high content of unsaturated bonds. Therefore, the shortage of polymeric materials with carboxyl groups, we open up many opportunities for their synthesis on the basis of cheap petrochemical raw materials. Major petroleum refineries and petrochemical enterprises have multi-tonnage waste of processes for the secondary processing of oil and its fractions, the so-called liquid pyrolysis products (RPP). Using oligomerization of such fractions, there are low molecular weight hydrocarbon oligomers known as hydrocarbon or petroleum polymer resins. RPP fractions contain more than half of unsaturated hydrocarbons, in particular, the fraction C_5, $C_{5\text{-}9}$, C_9 contains valuable diene monomers, such as: isoprene 20 ... 25, cyclopentadiene 20 ... 25, piperene 10 ... 15 and unsaturated aromatic and cyclic hydrocarbons, such as: 20 styrene, 15 vinyltoluenes, 10 indene, 10 dicyclopentadiene by % weight. Their number depends on the nature of the raw material: gaseous or liquid hydrocarbons, and the conditions of the process, and therefore varies in a fairly wide range of 45 ... 75 % by weight [1, 2].

The process of modification of hudrocarbon olygomers (HOs) can be carried out both on a periodic basis (with low volumes in per unit) and on a continuous (at multi-tonnage in-vah) scheme. The replacement of the periodic process by continuous intensifies it, promotes productivity, improves the quality of products and working conditions. Periodic processes are characterized by the fact that the raw material is loaded into the apparatus for a certain time, there is a series of stages of processing in it, and then the product is unloaded. These processes have a number of disadvantages: a change in the time parameters of the technological regime, which impairs the quality of the product; low productivity; the duration of the whole process is greater than continuous; energy costs higher due to heat losses during loading and unloading periods; periodic processes are difficult to mechanize and automate. But they also have advantages: they are characterized by great flexibility, the reactor of periodic action involves less investment than a reactor operating in continuous mode.

In continuous processes, the supply of raw materials and unloading of products is carried out continuously. In these processes there are no disadvantages characteristic of periodic processes. The continuous process differs in the stability of the parameters of the technological regime (temperature, pressure, concentration of substances, etc.), which, as a rule, improves the quality of products and allows to automate the process. In order to obtain modified HOs, it is proposed to use existing equipment of the periodic production process of petroleum resins by initiated oligomerization at JSC ORIANA (Kalush, Ivano-Frankivsk oblast) with additional equipment with its node for chemical modification of the finished HOs. The block scheme of the process of chemical modification of the finished HOs is shown in Fig. 1.

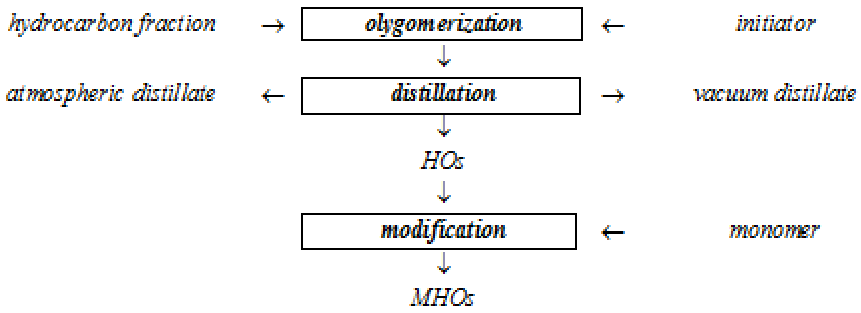

Fig. 1. Block scheme of chemical modification of hydrocarbon oligomers

Regarding the periodic process of co-oligomerization, it allows somewhat simplifying the technology of obtaining HOs with functional groups, reducing the number of stages of the process and thereby reducing the amount of process equipment. The modifier in this case is introduced directly into the reactor-polymerizer to the fraction and the initiator. Synthesis of functionalized HOs with oligomerisation of the hydrocarbon fraction C9 RPP with a comonomer allows it to be obtained by continuous process. An analogue of the continuous production of HOs by the thermal oligomerization of the unsaturated RPP fractions exists at JSC LINOS (Lysychansk, Lugansk oblast). In the technological scheme it is additionally necessary to provide comonomer and initiator supply lines, as shown in Fig. 2.

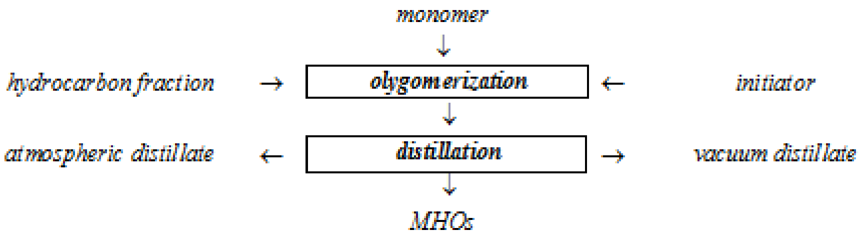

Fig. 2. Block scheme of olygomerization of hydrocarbon oligomers

Conclusion

As a result of experimental researches, functionalized hydrocarbon oligomers were obtained and the technology of their production on the industrial scale was proposed. The main technological aspects, which do not require significant investments and can be implemented without significant efforts, are worked out. By-products of production namely distillates, are also used as solvents in the paint and varnish industry, as well as components of boiler fuel.

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Quantitative Determination of Substances that Determine the Aroma of the Extract of a Bay Leaf

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Abstract* – *It is established that during the chladone extraction of the bay leaves the color, smell and taste of the original plant material are preserved. The number of flavors of the chladone extracts of the bay leaf after the first and second extractions has been determined. It was shown that the content of aromatics in chladone extracts of the bay leaf is 3,6 ... 4,8 times more in comparison with water-alcoholic extracts.

Keywords – bay leaf, additive, flavor number, liquified chladoni, extract.

Introduction

Laurel noble - a subtropical tree or shrub, all of which contain essential oils, tannins, resins, bitterness, which give them a typical aromatic odor and a pleasantly bitter taste. The composition of the bay leaf includes carbohydrates, fats, proteins, edible fibers, saturated fatty acids, vitamin C, macronutrients (calcium, magnesium, potassium, phosphorus) and trace elements (iron, zinc, copper, manganese) [1]. The content of essential oil in the leaves reaches 5.5%. The essential oil of the noble Laurel includes pineapple, cineole, myrcene, limonene, camphor, linalool, organic acids and other components [2-4].

The valuable chemical composition of the bay leaf causes its use in various food technologies. The prospect of using the water extract of a laurel leaf in the technology of bakery products as enrichers of the nutrient medium for the development and fermentation activity of yeast cells has been proven. The possibility of using a water-alcohol extract of a bay leaf as a natural antioxidant has been proven for the stabilization of carotenoids during the development of the technology of carotenoid additives in the form of finely divided powders [5]. It was shown that extraction of bay leaf with unrefined sunflower oil allows to obtain a spice-oil mixture with antibiotic activity [6]. The use of this mixture in food technology will stabilize microbiological processes while storing products.

Essential oil of the noble laurel is used during the production of sausage products, which allows not only to give them a pleasant aroma, but also to reduce the total number of foreign microorganisms and to restrain the process of oxidation of lipids during storage [7].

Analysis of Literary Data and Problem Statement

The main ways to get a laurel oil - is parodystillation and extraction with organic solvents. In the process of parodystillation, a significant disadvantage is the partial or complete destruction of thermolibious components at high temperature. The disadvantage of extraction with organic solvents is the chemical aggressiveness of solvents and the issue of removal of solvent residues from the final product is inevitable, which leads to additional costs and an increase in the complexity of the technology. Therefore, it is important to search for alternative methods of obtaining essential oils, free from undesirable impurities, which store their composition, as close as possible to the native [8].

Liquefied gases, like solvents, are increasingly used to produce high-quality lipid extracts from different biological sources. This is due to the significant technological advantages of this method and the fact that the extracts completely preserve the native structure of the molecules, taste and aromatic qualitative indices of the raw material and contain less foreign impurities. Chladone extraction technologies, having a high extraction ability, allows the removal of a wide range of biological active substances and change the composition of the resulting fractions, which is especially important in the production of food products [9-10].

Liquified refrigerants, with a viscosity less than in traditional solvents, are characterized as extractants with the best diffusion properties. In chemical terms, they are indifferent to the lipid fractions that secrete. They are Non-toxic and fire- and explosion-proof. The low values of the heat of evaporation and the boiling point of liquefied gases allows you to quickly remove the gas from the extracts at a low temperature, which ensures the preservation of thermolabel molecular complexes in the final product [11].

The purpose of the work was to quantitatively determine the substances that determine the aroma of the cold-extract extract of the bay leaf.

Results and Discussion

For the manufacture of the extract, dried leaves of the noble laurel, which grow in Georgia, were used. Technological stages of the process of chladone extraction included: preliminary crushing of the bay leaf to 250 microns, mixing with the chladone solvent in the extraction tank, extracting the extract in the process of diffusion, draining miscella of the dissolved extract, evaporating the solvent from the miscella, draining the laurel oil into the receiving vessel and sedimentationing for removing the fines of finely divided meal. As result we obtained the first chladone extract of a bay leaf. To obtain the second extract, it was used the meal of the bay leaf after the first extraction. Results of determination of organoleptic parameters of the quality of bay leaf chladone extracts are given in Table 1.

Table 1

Characteristics of the quality of the extract of the bay leaf

Name of the indicator	Characteristics that value	
	1	2
Appearance	Viscous substance	
Color	Green	
Taste, smell	Well expressed, characteristic of a bay leaf, without any foreign smell and taste	

One of the quantitative characteristics of the substance content that determines the aroma of raw materials and food products is the number of flavors conventionally expressed in milliliters of sodium trioxoethiosulfate per 100 g of product. To determine the total content of substances that determine the aroma of chladone extract bay leaf, the method of determining the number of aromas given in GHOST 8756.7-70 has been adapted. The basis for determining the amount of aroma is the reaction of the interaction of essential oils with a chromium blend, during which their oxidation occurs.

Substances causing the aroma of the extract of a bay leaf were discharged with a water vapor in a chimney receiving chamber. The resulting distillate was boiled in a water bath for 1 hour, after which it was cooled, 25 ml of a 10% solution of potassium iodide were added and left for 3 minutes in the dark. The iodine, which was isolated, was titrated with 0,2 N sodium trioxide thiosulfate solution. As a result of titration, the number of flavors was calculated.

It was found that the number of fragrances for the first and second chladone extraction of bay leaf is 1122 ± 20 ml and 833 ± 17 ml $Na_2S_2O_3$ / 100 g, respectively. The obtained values are exaggerated in 3.6 ... 4.8 times the value of this indicator for aqueous-alcoholic extract [5].

Conclusion

Thus, during the chladone extraction of the laurel leaves, the color, smell and taste of the original plant material are preserved. It was shown that carrying out extraction of a bay leaf with the help of chladones allows to obtain an extract with a higher content of aroma-forming substances in comparison with water-alcohol extraction. It is determined that the content of aromatics in the second chladone extract is sufficiently high, due to incomplete extraction of these substances during the first extraction. Therefore, further work will be carried out in the direction of establishing optimal regimes of the chladone extracting of bay leaves.

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Method of Obtaining Malt Extracts

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Abstract* – The work substantiates the expediency of using low-frequency mechanical vibrations for intensifying the extraction of target components from raw materials of grain origin. Optimal conditions and operating modes of the vibroextractor of periodic action for producing malt extracts are presented. The technology of obtaining dry malt extracts using the vibration extractor is given.

Keywords – extraction, liquid-solid system, vibroextractor, malt, grain..

Introduction

Today, the market of dietary supplements is developing more rapidly, so obtaining an extract of malt plant materials with a high content of biologically active substances, and then entering it into foods, dietary supplements and cosmetics is relevant.

Among products of increased biological value, malt of cereal crops - wheat, oats, barley and corn - occupies a special place. Sprouted grains (malt) contain the entire set of components necessary for a balanced diet - proteins, easily digestible carbohydrates, dietary fibers, minerals, vitamins. In addition, malt cereals contain coloring and polyphenolic compounds, as well as plant enzymes and hormones.

Extracts are widely used as fillers and fortifiers of products; therefore, it is advisable to extract target components from natural raw materials by extraction.

Materials and Methods

At present, the practical provision of conditions for the optimal conduct of the extraction process with traditional methods is complicated, on the one hand, by the named and other properties of the raw materials, on the other hand, by the process-technological and constructive possibilities of the existing extraction equipment. Therefore, one of the relatively effective ways to intensify the process of extraction is the use of intensive energy-saving hydrodynamic modes, which are provided by low-frequency mechanical vibrations of the system.

Traditional technologies of periodic solid-phase extraction accompanies a number of disadvantages, among which are compaction of the mass of the raw material being processed and its simultaneous movement with rotating mixing devices and the like. This leads to a decrease in the relative velocity of the phases and the screening of the particles among themselves and, consequently, to a decrease in their activity in the process of mass transfer. Reducing or even complete elimination of the screening effect can be accomplished in the extractor, the principle of which involves continuous surface renewal phase contact method overlay medium interacting field low-frequency mechanical vibrations. For this purpose, the vibroextractor used a new principle of creating powerful vibro-turbulant flows in the working volume using flexible perforated vibration mixing devices.

The design feature of this vibratory extractor is possible to create turbulent pulsating alternating flows directed both toward the periphery of the apparatus and to the central part thereof. The hydrodynamic properties of these streams determine their action as a turbulizing factor at the micro level and a macroscale factor that eliminates stagnant zones.

The extract was extracted from several types of malt grain mass, namely: wheat malt, barley malt and corn malt.

The purpose of grain germination is the synthesis and activation of enzymes, under the influence of which the complete dissolution of all reserve substances is achieved in the extraction process. The significant content of enzymes in germinated grains of cereals contributes to the splitting of carbohydrates into simple sugars, and proteins into amino acids, that is, high-molecular and low-molecular water-soluble substances. Particularly interested in free amino acids that are directly assimilated by the human body.

Even under the action of enzymes, during germination, part of the complex substances of the grain is converted into maltose, glucose, maltodextrin and dextrins, peptones, peptides, amino acids and others.

Results

The hydromodule was selected for each raw material individually, and the normal composition of the malt grinding was characterized by the following ratios of fractions%: shells 15-18, large grits 18-22, fine grits 30-35, flour 25-35. The ratio of fine grits and flour to large grits should be 3: 1, but not less than 2.5: 1. This is controlled by the excessive loss of the extract through the large grits.

The process is carried out, preventing contact with air. The optimal duration of the process is 255 minutes - for wheat malt (yield 3%); 210 minutes - for barley malt (yield 2%); 205 minutes - for corn malt (yield 2%). Longer time keeping the malt in water is not advisable, since it does not lead to a significant increase in the solids content of the extract.

The production method of malt extract includes the cleaning of raw materials, grinding, extraction using low-frequency mechanical vibrations at a frequency of 5 Hz, amplitude of 10 mm, for the optimum duration of the process for a certain raw material and the temperature of the extractant 60 -70 ° C and concentration. According to the technology, the vibrator-driven extractor has a vibration-turbulent mixing system. With a collection of filtered extract, the heater of the filtered extract is additionally connected in series, an evaporative unit, a collection of extract-liquid concentrate, a heater and dryer with a cyclone of an extract-liquid concentrate, powder extract concentrate conveyor, automatic machine for packing of extract concentrate powder, conveyor of packaged extract concentrate powder, and the collector-mixer of the meal of the extracted raw material and the sludge from the filtering centrifuge are additionally sequentially connected with the extractor and the filtering centrifuge, sludge press, sludge conveyor, sludge dryer with cyclone, dried sludge conveyor, automatic packaging machine for dried sludge and conveyor of packed sludge.

Conclusion

The use of such an extractor will provide a high intensity of the extraction process, shorten its duration and ensure the maximum yield of biologically active substances from the plant material by reducing the stagnant fluid layer and creating convective flows that facilitate the transfer of substances to the extractant.

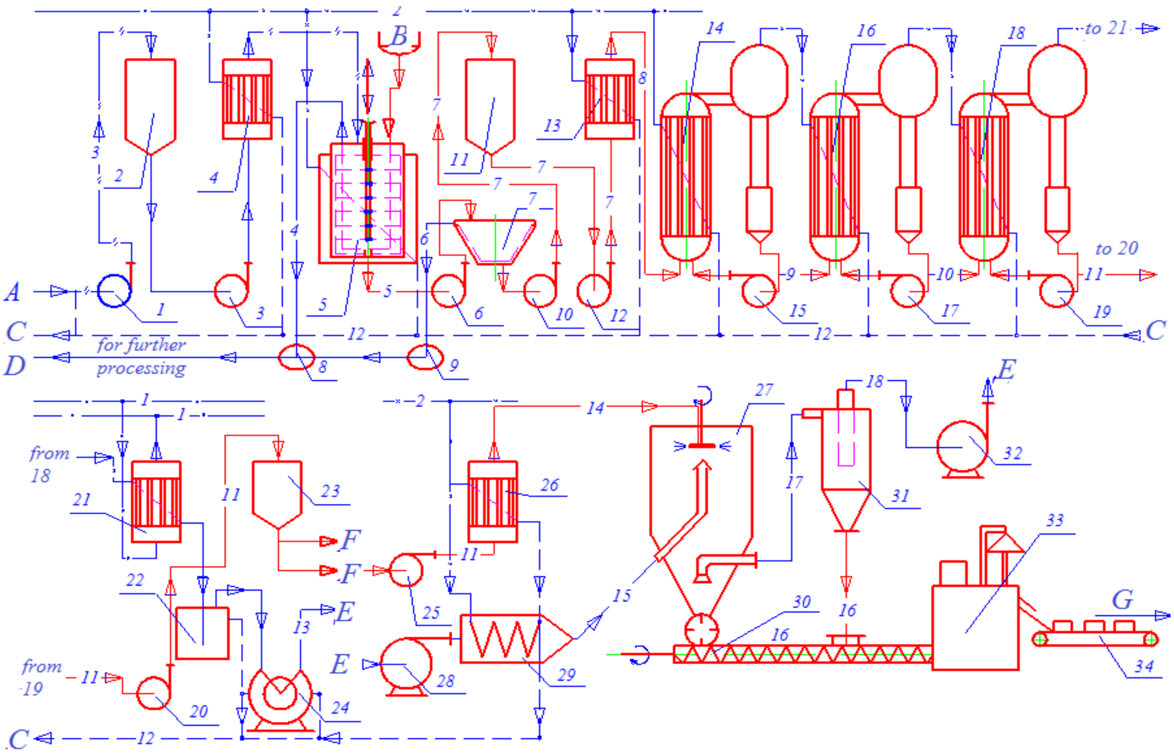

Fig.1. Hardware-technological scheme of production of extracts from plant raw materials by vibroextraction

2 - collector, 4 - heater of technological water - extractant, 5 - vibroextractor, 7 - centrifugal filter, 8 - collector of meal of extracted raw materials, 9 - collector of sludge from centrifuge, 11 - collector, 13 - filtered extract heater, 14, 16, 18 - three-body evaporator, 21 - secondary steam condenser, 22 - evacuated condensate collector, 23 - collector, 26 - concentrate heater, 1, 3, 6, 10, 12, 15, 17, 19, 20, 25 - centrifugal pumps, 24 - vacuum pump, 27 - spray dryer, 28, 32 - fans, 30, 34 - conveyors, 29 - heater, 31 - cyclone of spray dryer 33 - packing machine.

Thus, the modes of extraction of wheat, barley and corn malt were investigated, which allows to obtain high-value extracts from these types of raw materials for the cosmetic, food and pharmaceutical industries. Also developed a technology for producing malt extracts using vibroextraction equipment.

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Deep Eutectic Solvent Reline − Highly Efficient Electrolyte for Stainless Steel Electropolishing

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***Abstract* – New modern technology of surface treatment of stainless steel was shown. Deep eutectic solvent Reline was proposed as a highly efficient electrolyte for electropolishing of AISI 304. Anodic treatment of AISI 304 steel samples in Reline leads to an improvement in appearance and surface properties. Electropolished samples are characterized by low roughness, shiny surface, less wettability and as a consequence of higher resistance to corrosion.**

Keywords – deep eutectic solvent, eco-friendly medium, electropolishing, cyclic voltammogram, roughness coefficient, wettability, contact angle.

Introduction

Well known that electropolishing improves the near surface chemistry of stainless steel [1,2]. Not only does it remove embedded particles and inclusions, it also improves the atomic ratios of the material's alloying elements. Electropolishing preferentially dissolves Iron from the material and leaves the surface with a higher relative concentration of Chromium. Upon exposure to Oxygen, this improved surface will form a thicker and more uniform oxide layer with enhanced corrosion resistance properties. Electropolished stainless steels are better suited to resist the onset of pitting corrosion, crevice corrosion, stress corrosion cracking, and microbiologically influenced corrosion.

«Traditional» electropolishing technologies use toxic mixtures of chemicals - concentrated solutions of sulfuric, hydrochloric, orthophosphoric, hydrofluoric, nitric acids with the addition of glycols, chromic anhydride, etc [3-7]. Such kind of electrolytes capable of destroying industrial equipment, harming the environment and human health. Moreover, chemically aggressive mixtures are not always effective and do not lead to the necessary improvement in the quality of functional materials (metals and alloys).

Modern low temperature ionic liquids – deep eutectic solvents (DESs) can be perfect alternative for traditional toxic electropolishing electrolytes. For example such DES as Reline (eutectic mixture of choline chloride and urea with molar ratio 1:2 respectively) are not only environmentally friendly, but also possess a number of very attractive properties: chemical, thermal, electrochemical stability, availability of components, ease of synthesis and relatively high as for ionic liquids electrical conductivity at high viscosity [8-11].

A unique combination of high electrical conductivity with high viscosity allows predicting significant success in the use of this electrolyte for the anodic treatment of metals and alloys.

The main goal of this work is to use complex approach for study of the principle possibility of using Reline as an electrolyte for highly efficient anodic treatment of austenitic stainless steel AISI 304.

Experiment and Discussion

The cyclic voltammogram (CVA) obtained for stainless steel AISI 304 in deep eutectic solvent Reline at temperature 20oC is shown in Fig. 1. Scanning of potential was carried out from the stationary value -0.5 V in anodic region to the potential ≈ 9.5 V and then in cathodic region to the potential ≈ -3 V (potential scan rate was equal 2 mV/s). As can be seen from CVA, in anodic region noticeable peak of dissolving current of steel sample is observed, after can be seen a long "passive" region. Passivation of a metal sample can be associated with the formation of protective oxides on the surface of stainless steel. Passive chromium and nickel oxides (these elements are part of the alloy AISI 304) can be formed on the surface and prevent further sample dissolution.

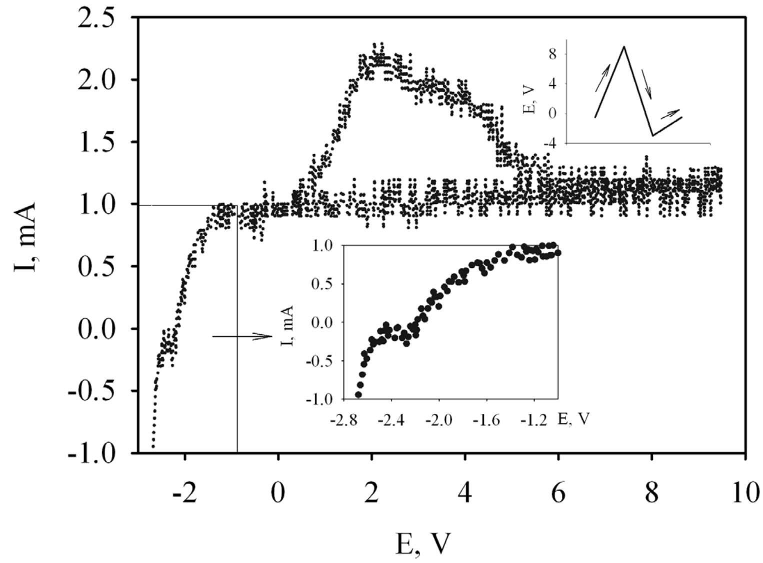


Fig.1. CVA of AISI 304 (s=4 cm2) in deep eutectic solvent Reline

In cathodic region (Fig. 1) peak of Fe2+→Fe0 electroreduction current is observed. Further increase of current corresponds to other electroreduction reactions for solvent components.

Based on information obtained from the CVA for the electropolishing process in potentiostatic mode several potential values were selected: 1, 1.5, 2, 4, 6 and 8 V. Image that illustrated of 20 minutes electropolishing effect for AISI 304 samples at selected potentials is shown in Fig. 2

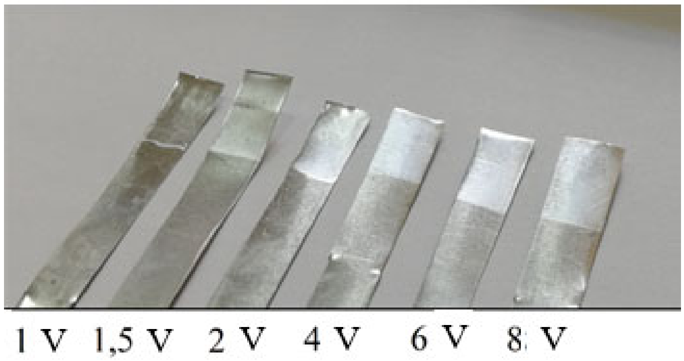
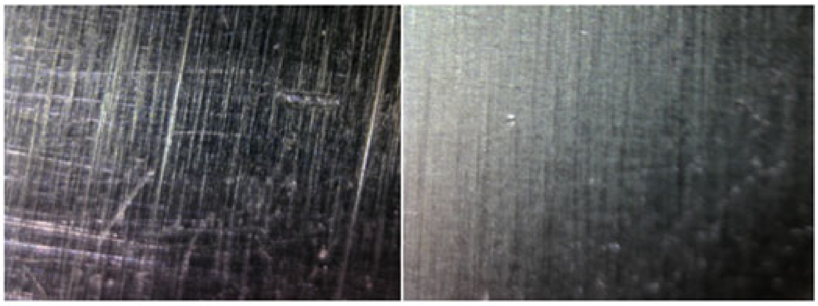


Fig. 2. AISI 304 samples after the electroplating process at different potentials in Reline solvent (processing time 20 min.)

As can be seen from Fig. 2 with the increase of the electroplating potential the surface of the samples becomes shinier. When polishing potential E ≥ 2 V the surface of AISI 304 samples acquires an attractive silver-gray tint. It shod be noted that after electropolishing of AISI 304 samples, not only the appearance of the surface changes, but also the properties.

Electropolishing of stainless steel samples (AISI 304) in Reline solvent leads to a decrease in surface roughness (Fig. 3). During the anodic process dissolution of irregularities and other defects take place; deep scratches and traces of rolled steel sheet disappeared after polishing treatment.

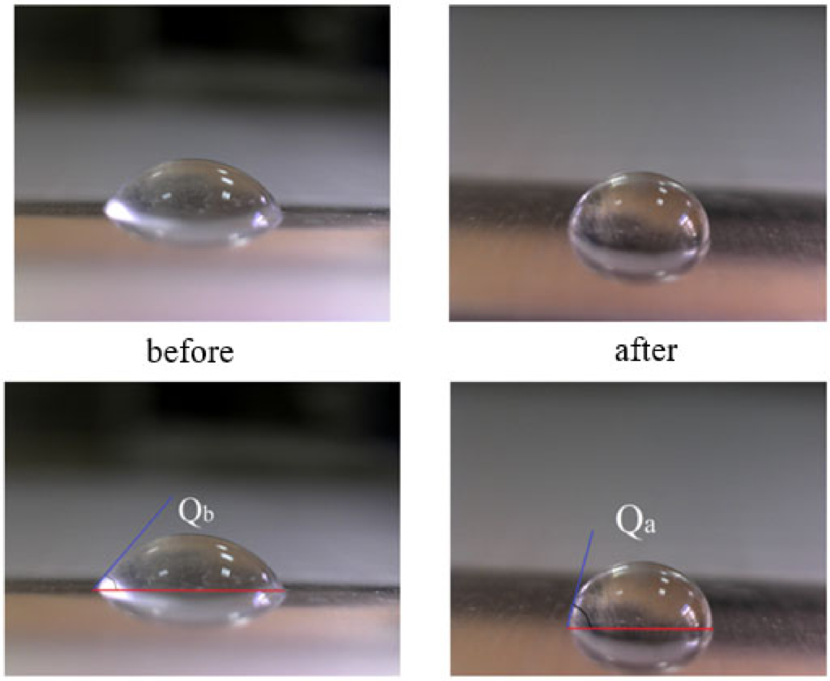
Moreover it can be argued that changes in the surface layer of the samples associated with changes in the surface composition of the alloy.



before after

Fig. 3. Optical microscope SyperEyes B800 (×500) photo of AISI 304 sample before and after the electropolishing process in Reline (τ = 20 min., E = 8 V)

Changes in wettability properties of AISI 304 surface after the polishing process was found (see Fig. 4). As can be seen from Fig. 4, the shape of water drop on unpolished and polished surface is noticeably different. Contact angle for AISI 304 polished sample is about 2 times more than contact angle for unpolished sample.



before after

Fig. 4. A drop of distilled water on unpolished (before) and polished (after) surface of AISI 304 in Reline (electropolishing conditions τ = 20 min., E = 8 V)

Thus, electropolishing of stainless steel leads to an increase in the hydrophobic properties of AISI 304 surface. As a rule, an increase in the surface hydrophobicity may lead to an improvement in the corrosion resistance of the material. Therefore, it should be expected that AISI 304 stainless stee after electropolishing in Reline will be more resistant to corrosion than unpolished.

Conclusion

It was shown that environmentally friendly electrolyte Reline can be used as a promising alternative to traditional toxic stainless steel polishing electrolytes. AISI 304 samples after polishing in Reline are characterized not only by a uniform shiny surface, but also by improved functional properties. This type of anodic treatment helps to decrease the surface roughness of stainless steel, increase hydrophobicity and improve corrosion resistance.

Acknowledgments

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Application of Immobilized Yeast Cells in Fermentation of Sugar-Based Raw Materials for the Production of Bioethanol

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Abstract* – *This abstract describes a study of efficiency immobilized yeasts usage in the fermentation of sugar-based raw materials. It was found that the fermentation of molasses wort by yeasts immobilized in sorghum stalks particles provides an increase in the ethanol production rate per gram of biomass per hour, increases the yield of ethanol per ton of raw materials, as well as reduces the fermentation time. It is proved that this technological method could improve the bioethanol production efficiency.

Keywords – fermentation, molasses, Saccharomyces cerevisiae, bioethanol, immobilized yeasts.

Introduction

According to the current technology, the processing of sugar-based raw materials into bioethanol is accompanied by the synthesis of biomass in the amount of 18 - 22 g/dm3, which is inactivated during the wort distillation process and removed from the production cycle with the vinasse.

The disadvantages of such technology are the sugar losses for the synthesis of biomass and the increase of the sewage pollution degree and human pressure on the environment, which is eliminated by yeasts immobilizing on different types of carriers in the fermentation zone. The system of immobilized cells helps to increase the process capacity, makes it possible to reuse biomass during a certain number of cycles and reduce costs for the production of the final product [1].

Production simplicity, high mechanical resistance, high degree of renewing, long life and low cost are advantages for using cellulose-containing raw material as an agent for immobilization.

The distribution of cultivation of sugar sorghum as a raw material for the production of syrups and ethanol in recent years in Ukraine creates the conditions for use of the crushed stalks as a matrix for the microorganisms immobilization [2], [3].

The purpose of research is to investigate technological parameters of yeasts cells immobilized on a sweet sorghum stalks matrix using in the continuous process of fermentation of wort based on sugar-beet molasses.

Materials and Methods

Alcoholic yeasts K-7 were used as an ethanol producent. The wort from sugar beet molasses, obtained from the technological process, with the concentration of 24.6% solids, was used as a substrate. Dry sorghum stalk were crushed to particles 7 * 8 * 8 mm, sterilized and used as immobilization matrix. Immobilization of yeast cells on the matrix was carried out using medium with an initial concentration of dry matter of 12% and biomass content of 18 - 20 g/ dm3. The process continued until the maximum saturation of sorption carrier surface. Continuous fermentation was carried out at the medium dilution rate 0.037 h. -1.

Results

To determine the efficiency of continuous wort fermentation using immobilized yeast the method of "fermentation probe" was used, with identical concentration and under identical conditions. Data from studies are given in Table 1.

Table 1

The fermentation of molasses wort with concentration of 24.6% of solids by a continuous method using immobilized yeasts and by "fermentation probe"

Indicator	The method of fermentation	
	Fermentation probe	Continuous method using immobilized yeast
Sugar put with a wort, g/dm^3	149,38	149,38
Biomass content, g/dm^3	17,50	32,80
Ethanol contetnt, %w/w.	9,18	9,50
Non-fermented sugar contetnt, g/dm^3	14,07	8,29
Duration of process, hours	80,0	29,3
Ethanol production rate, cm^3/g biomass per hour	0,066	0,099
Product yield per ton of raw materials, dal	30,97	32,05

For equal content of digestible sugars in the wort, the usage of immobilized yeast provides an ethanol content in the mature wort increase of more than 3.5% relative, and the content of non-fermented sugar lower by 41.1% compared with the "fermentation test". Under the conditions of high concentration of a fermented sugars (14.9%) and non-sugars (9.7%) in molasses wort immobilized yeasts are characterized by a higher ethanol production rate.

The use of immobilized yeast in the continuous fermentation of molasses wort increases the ethanol production rate by 30% per 1 g of biomass, the yield of ethanol by 1.08 dal per ton of raw materials and shortens the duration of the fermentation process.

Conclusion

The advantages of using immobilized yeast cells in the continuous process of fermentation of sugar-based raw materials are proven, which is a promising direction of development of technological support for bioethanol production and increase of its efficiency.

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Polylactide Composites with Finely Divided Fillers

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***Abstract* – Polymer composite materials based on polylactide and fillers of various nature (hydroxyapatite and modified metal-containing silicates) have been obtained. It has been found the properties of the developed materials: melt flow index, Vicat softening point and the surface hardness vary depending on the content and nature of the filler.**

Keywords – polylactide, hydroxyapatite, silicate, filler, composite.

Introduction

The development of industry needs the use of new polymer materials with a set of required characteristics. The increased attention is paid to the environmental safety of such materials, in particular regarding the use of renewable sources of raw materials for their obtaining and the ability to biodegradate. In this regard, the promising material is polylactide (PLA).

Experimental

PLA is a biodegradable thermoplastic aliphatic polyester with lactic acid monomer. Fillers hydroxyapatite (HA) and modified metal-containing silicates fillers (Ni-SF) [1] were used for the preparation of PLA composites. To obtain composites, mixing of loose components in a drum type mixer and homogenization of the mixture in a Cellier extruder was carried out.

Results and Discussion

The introduction of HA in the PLA leads to a decrease in material fluidity, in particular the value of the melt flow index (MFI 210 ˚C, 2.16 kg). Adding 1% by weight. HA reduces the value of the MFI to 21 g/10 min, MFI of unfilled PLA - 27.2 g/10 min. Further increase in the content of HA to 2, 5, 10 and 20% by wt. naturally reduces the value of MFI of composite to 16.5, 11.8, 8.2 and 6.7 g/10 min, respectively. It should be noted that HA behaves like a classic inert filler, which is also confirmed by its influence on Vicat softening point of received materials. In particular, unfilled PLA is characterized of Vicat softening point 68.6 °C and the adding of HA slightly reduces it, with a minimum 65.4 °C at filling 5% by wt. Adding of HA increases the value of surface hardness of PLA, which is obviously due to the reduction of free space between the macromolecules of PLA and as a consequence of the decrease of high-elastice deformation of the surface layers of PLA. Other influences have modified Ni-SF, MFI of PLA with 10 % by wt. Ni-SF is 19.3 g/10 min and for modified Ni-SF by polyvinyl alcohol and polyvinylpyrrolidone 13.2 and 25.2 g/10 min, respectively. This is due to the interaction between the PLA macromolecules and the functional groups of silicate fillers and modifiers.

Conclusion

Based on the performed studies polylactide composites can be further processed into product by injection molding, extrusion and 3D printing.

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Innovative Method and Installation for Heating and Melting Bases for the Production of Suppositories

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***Abstract* – The method for the thermal contact heating and melting of ointment bases for the manufacture of soft dosage forms at pharmaceutical companies is presented and the installation for its implementation is developed.**

Keywords – heat exchange processes, heating, melting, ointment base, intensification.

Introduction

Suppositories are becoming more common in pharmacy and medicine due to the high rate of absorption of drugs and the possibility of combining ingredients with different pharmacological, physical and chemical properties in suppositories. Suppository dosage forms (DF) in the pharmaceutical market of Ukraine are now represented in most foreign pharmaceutical companies (leaders are from: Germany, France, Italy and Switzerland) and a small number of domestic companies: Lekhim (Kharkiv), Monfarm (Monastyrishche), “FITOLEK” (Kharkiv), Sperko Ukraine (Vinnitsa), Pharmex Group (Borispol) [1]. Out-of-date technologies and equipment for the manufacture of suppositories are the reason for the purchase and operation of imported equipment from Germany, Italy, the USA and other countries. The necessity for development and implementation high-performance innovative technologies and equipment for the production of suppository dosage forms (DF) is due to the demand of the people in domestic pharmaceutical preparations.

Main Material

Suppositories from the physico-chemical point of view are considered as dispersed systems consisting of a dispersed medium, represented by a base, and a dispersed phase, in the role of which medicinal substances act. Suppositories are complex multicomponent heterogeneous systems, since they contain one or more drugs dispersed or dissolved in a simple or complex basis.

The technology of production of suppository DF includes a complex of heat and mass transfer processes: heat transfer during heating, cooling and melting; stirring and dissolving; dispersion (increase of phase interface) and homogenization; structuring (obtaining a bundle-disperse system); extraction (convective and molecular diffusion, as well as transfer of matter from solid to liquid phase).

An important stage for obtaining suppository DF is the preparation of suppository bases. Hydrophobic and hydrophilic bases and their mixtures are used depending on the pharmacological action of suppositories. Some problems arise when obtaining stable diphilic bases containing hydrophilic and hydrophobic parts, but such bases give the opportunity to introduce into them both fatty and water-soluble medicinal substances and their solutions.

The importance and role of the bases for suppositories are important and diverse. The bases provide the necessary mass of suppositories and, accordingly, the proper concentration of medicinal substances, a soft consistency, significantly affect their stability. The degree of release of drugs from suppositories, the speed and completeness of their absorption in many respects depend on the nature, composition and properties of the base.

Reactors with different types of mixers (Fig. 1, a), bathtubs with coils (Fig. 1, b), electric heaters, heating chambers, etc. are used according to the traditional technology for heating and melting of bases in pharmaceutical factories. But these methods have a number of significant disadvantages: labor-intensive and energy-consuming; possible overheating of the base, which leads to various changes in the physical-chemical and structural-mechanical properties of the dispersion phase; occurrence of contamination; not uniform heating of the whole mass of the base. For example, overheating of fats and fatty substances often leads to the formation of such forms that have lower melting temperatures, as well as suppositories after overheating of the base are unstable during storage, since they are melted at room temperature. In this case, the substances lose their hardness, which excludes the possibility of manufacturing suppositories.

A method of thermal contact melting through contact and convective heat transfer, which allows to intensify the process and reduce energy costs is developed in the Institute of Engineering Termophysics [2-4]. The principle of the method for melting the suppository base in cylindrical container is on the movement of the heating disc under the action of gravity during the melting and flow of the molten base through the gaps between the disc and the walls of the container. The difference between the proposed method and the existing one is to bring energy directly to the front of the phase transformation with the help of the heating disc that contacts the outer boundary of the unmelting substance. The method allows to heat and melt only that part of the base, which is necessary. It is possible to realize the controlled melting process, which enables more efficient use of energy. In this case, the temperature of the disc heater in the base contact area is lower than the temperature of its destruction. The melting occurs due to convective heat transfer from the upper surface of the heater in the molten mass.

An installation for thermo-contact heating and melting was developed on the basis of the proposed method (Fig. 1, c). The installation combines three technological operations: melting, unloading and dosage, and besides energy efficiency, can save time and human resources.

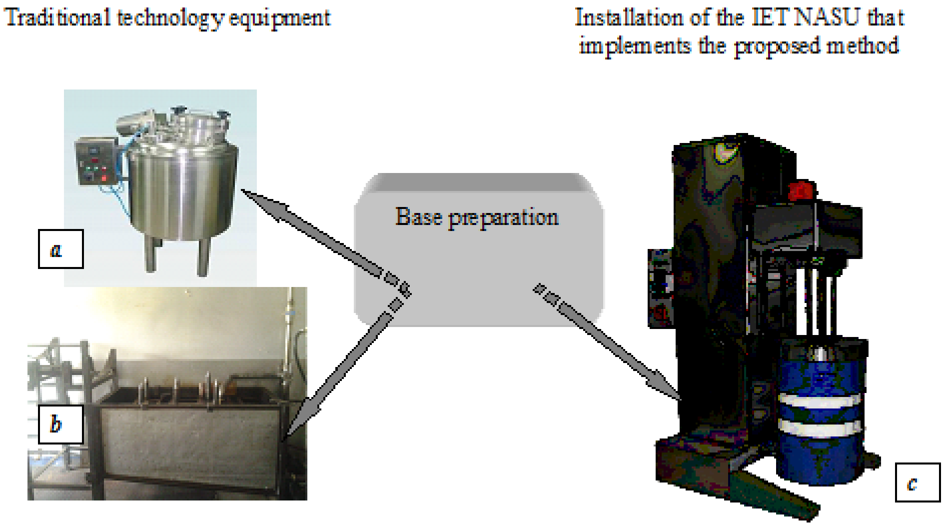
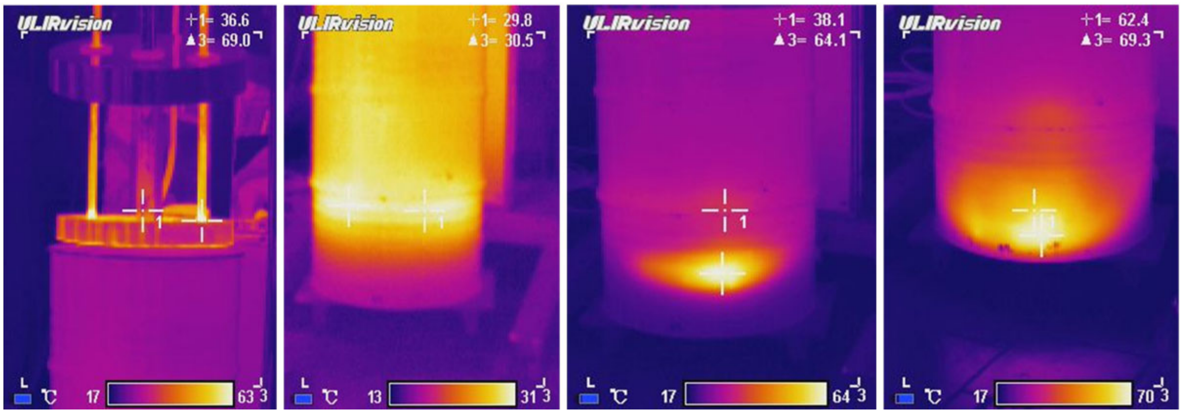


Fig.1. Equipment for heating and melting bases for the manufacture of suppositories: a) a reactor with a mixers; b) bathtub with coil; c) “Thermobat” type installation.

Using thermal imager Ti-160 it was possible to trace the movement of the heater along the length of the container, as well as the temperature distribution on the surface of the thermo-contact heater and inside the metal drums of the manufacturer (Fig. 2). Thermograms show uniform heat-up of the thermo-contact heater (Fig. 2, a) and the total volume of the melt as it moves to the bottom of the drum and melt the base (Fig. 2, b-d). Due to the low coefficient of thermal conductivity, the base is in the initial viscous state, and it is heated and melted in contact with the heater (Fig. 2, c). At the end of the process (Fig. 2, d), convection flows are observed, which helps maintain the temperature of the melt at a given level.



a) b) c) d)

Fig. 2. Thermograms of thermo-contact heating process and melting of bases in the drums of the manufacturer:

a) heat up of the thermo-contact heater; b) the beginning of heating and melting; c) heating in the process of lowering the thermo-contact heater; d) the end of heating and melting (the thermo-contact heater drops to the bottom of the drum).

The developed method and the installation for thermo-contact heating and melting allow to melt the required amount of base quickly and efficiently (Figs. 3 and 4) for transportation to the next stages of the manufacture of suppositories. “Thermobat” type installation, which correspond to GMP standards, was developed and implemented at pharmaceutical factories: UC “Pharmacy”, “Lugansk Pharmaceutical Factory”, Lugansk; JSC “Riga Pharmaceutical Factory”, Riga; LLC “Ternofarm”, Ternopil.

Fig. 3. White pharmaceutical MERKUR 500 (Germany).

Fig. 4. Molten vaseline on installation “Thermobat -M”.

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Analytical and Experimental Modeling of Heat and Mass Transfer in Electrodynamic Apparatuses

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***Abstract* – The hypothesis of possibility of electromagnetic energy sources using for address energy delivery directly to grout moisture is offering. The schemes of fuel energy conversion during traditional thermal concentration technology and innovation plant based on the electromagnetic energy generators are presented.**

Keywords – nanotechnologies, microwave field, mechanodiffusion effect, math modeling, address energy delivery.

Introduction

Traditional technologies of drying and evaporation of chemical, pharmaceutical and food industries do not meet the modern requirements of resource-energy efficiency. The processes associated with the dehydration of raw materials are characterized by common serious problems: high energy consumption and quality of the finished product, especially for thermolabile raw materials. An independent problem of evaporators is the regulation of the finished product final concentration. This problem is due to the fact that with increasing concentration of the solution, its viscosity and the thickness of the boundary thermal layer increase. The result is a decrease of the steam generation intensity, thermal deterioration of raw materials in the boundary layer. The task of the work is to substantiate the prospects of fundamentally new methods of organizing the dehydration processes in the electrodynamic apparatuses developed in the ONAFT.

Research Results

Electrodynamic apparatus designs implement the scientific and technical hypothesis proposed by the authors: "the processing of raw materials, which contain polar molecules, with an electromagnetic field will lead to the selective energy action directly on polar molecules, partial transfer of liquid into the vapor phase, increase of pressure in the volume of raw materials and initiate a specific hydrodynamic flow, the power of which can exceed the traditional diffusion flux by orders of magnitude ".

The task is to develop a mathematical model for the interaction of a microwave electromagnetic field with a liquid in a capillary 1 (Fig. 1). The energy supply N is volume at the PG of the second kind. The modeling is based on the first law of thermodynamics and the Fourier-Kirchhoff equations, which reflect the thermal interactions between the elements of the system under consideration. Since the work done by the body, in accordance with the problem posed, is zero, the first law of thermodynamics for this case will be written in the form:

$$Q_{st} + Q_V = \Delta U \qquad (1)$$

where Qst is the amount of heat received (or given) by the body through the surface of the capillary (S); QV is the amount of heat that is absorbed by the solution from electromagnetic energy sources; ΔU – change of internal energy.

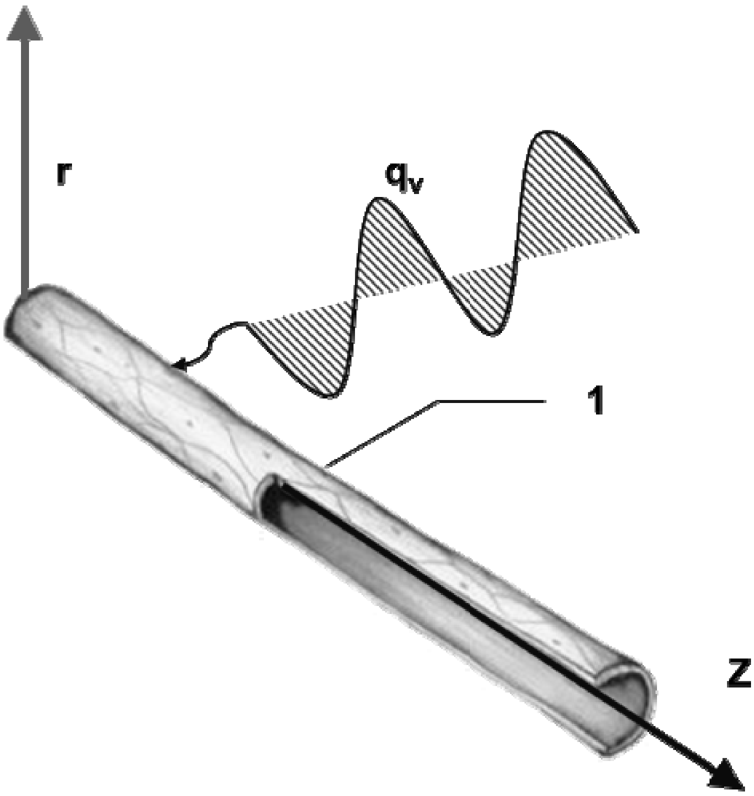

Fig.1. Statement of the modeling problem.

Experimental studies were carried out at the stand (Fig. 2), the main units of which are: evaporator chamber, chamber body, raw material, vacuum pump, condenser (CD), water cooler, a condensate collector (CC) and a scale.

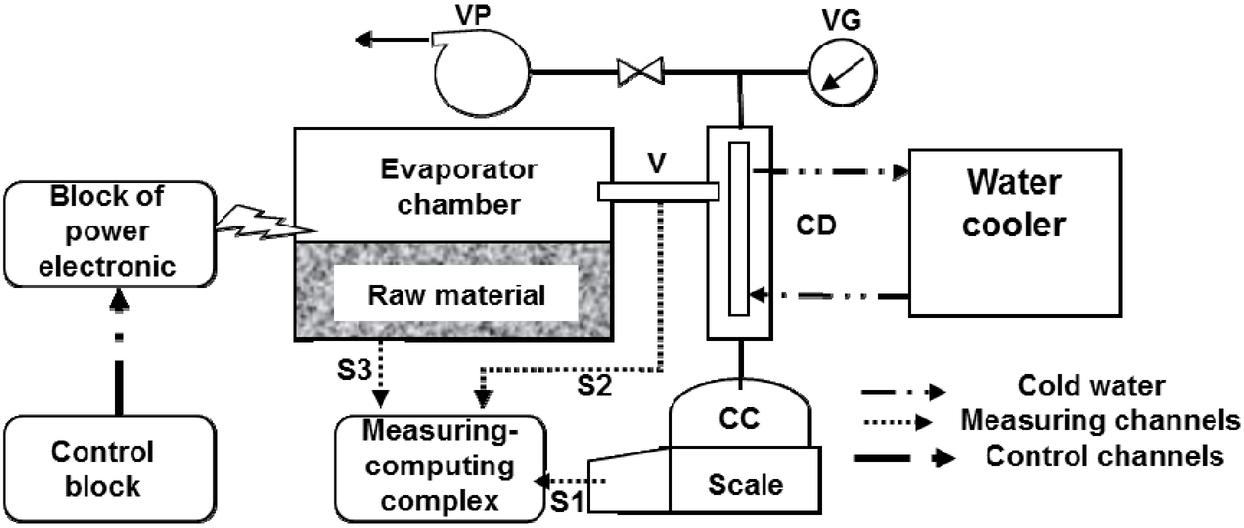

Fig.2. Scheme of the experimental stand.

In the experiments, the following were recorded: power consumption, vacuum, product temperature and steam output. The current values of W were determined from the indications of electronic scales (by the mass of the condensate in the collection). Thus, the yield of steam was determined with high accuracy. Operating temperatures did not exceed 50 °C. Typical dependencies are shown in Fig. 3.

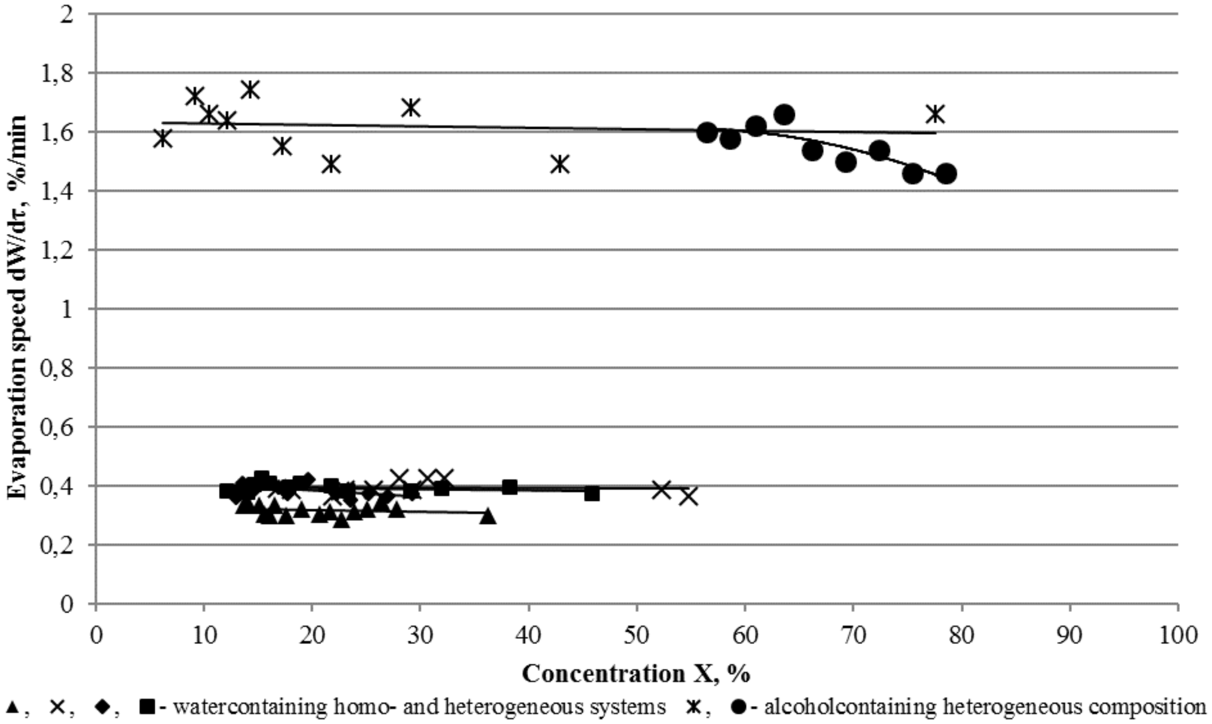

Fig.3. Lines of vaporization rate in electrodynamic apparatus.

Conclusion

In the conditions of EMF it is possible to initiate a specific flow from the volume of raw material. This effect was recorded for the first time; it was given the name "mechanodiffusion effect". The organization of such a flow, the driving force of which is the pressure difference, allows you to remove moisture in the form of mist during drying, that is, not convert all the moisture into steam, significantly reduce both energy costs and the duration of the process. The result of such processes can be: increase in the yield of target components, the transition to a solution of valuable components that were not removed by traditional methods (aromatic and flavor complexes, compounds).

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Thermodynamics of Ortophosphoric Acid Adsorption Under Static Conditions

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Abstract* – *The adsorption of ortophosphoric acid by natural zeolite under static conditions has been investigated. The significant increasein zeolite sorption capacity was observed while interactionof zeolite and wastewaters with acid reaction.The thermodynamic calculations of the polymolecular adsorption have been carried out.

Keywords – adsorption, thermodynamics, phosphates, zeolite, BET isotherm.

Introduction

In the previous publication, the results of experimental studies of adsorption of phosphates with natural zeolite were presented. It was found that in the range of concentrations above 180 mg / dm3 was a sharp increase of the sorption capacity of zeolite. However, the mechanism of this phenomenon was not clear [1]. therefore our task was to establish the thermodynamic probability of polymolecular adsorption of orthophosphoric acid by zeolite.

Experimental

A graphical interpretation of the experimental data on the adsorption of orthophosphoric acid with natural zeolite by the BET isotherm for the area of initial concentrations up to 375 mg / dm3 is presented on Fig. 1. Therefore our task was to establish the thermodynamic probability of polymolecular adsorption of orthophosphoric acid by zeolite.

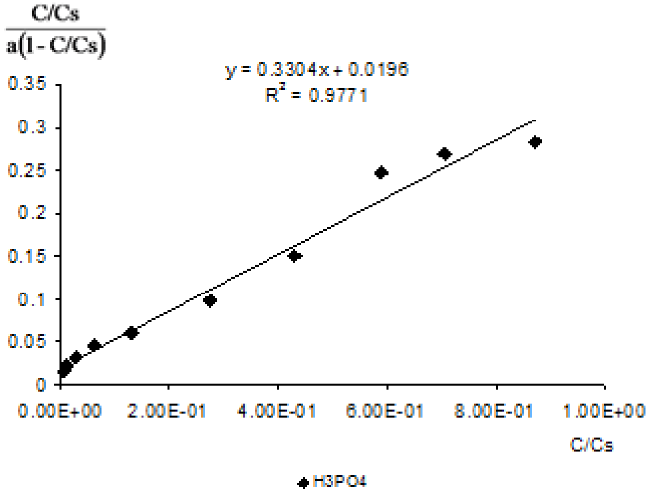

Fig. 1 - Linearized BET isotherm for adsorption of orthophosphoric acid by natural zeolite

Parameters of the BET equation for the phosphate adsorption process by zeolite $\frac{1}{a_m K}=0.0196$; $\frac{K-1}{a_m K}=0.3304$; K=0.99352416; the maximum value of adsorption capacity on phosphates in multimolecular layer am=51.35296. Taking into account that the experimental data are well interpreted by the BET equation (determination coefficient R2=0.9771), we can assume formation in the volume of zeolite polyphosphates according to the equation:

$$3H_3PO_4 + 3NaOH \rightarrow Na_5P_3O_{10} + 7H_2O \qquad (1)$$

To confirm the formation of polyphosphates in the volume of the sorbent, we have calculated the change in the standard Gibbs energy.

$$\Delta G_0^{298} = \Delta \mathrm{H}_0^{298} - T\Delta S_0^{298} \ \frac{kJ}{mol} \qquad (2)$$

where ΔG_0^{298}- Gibbs energy change, J / (mol); ΔS_0^{298}- entropy change, J / (mole · K); ΔH_0^{298}- enthalpy change, J / (mole); T-absolute temperature, K.

The equilibrium state of the thermodynamic system is function of entropy and enthalpy factors. With the temperature T = dH / dS, the system will be in equilibrium [2].

Entropy change we calculated according to the following equation:

$$\Delta \mathrm{S}_0^{298} = \sum \Delta \mathrm{S}_{0\ \text{п.р}}^{298} - \sum \Delta \mathrm{S}_{0\ \text{вих}}^{298},\ \frac{kJ}{mol \cdot K} \qquad (3)$$

According to Hess's law we calculate the heat effect:

$$\Delta H_0^{298} = \sum \Delta H_{0\ \mathrm{p}}^{298} - \sum \Delta H_{0\ \mathrm{s}}^{298},\ \frac{kJ}{mol} \qquad (4)$$

Under standard conditions (T = 298 K), the change in Gibbs energy also depends on the ratio of enthalpy and entropy factors [2].

The calculation of the thermodynamic parameters according to these equations are given in Table 1.

Table 1

Computation result of thermodynamic parameters of polymolecular adsorption of phosphates

Type of substance	Compound	Stoichio-metric coefficient	ΔH°298, kJ / mol	ΔS°298, kJ / mol K	ΔG, kJ / mol t=298 K	equilibrium temperature, К teq=dH/dS
Reaction product	$Na_5P_3O_{10}$	1	-4409	0.381	-	-
Reaction product	H_2O	7	-285.8	0.07	-	-
Reagent	NaOH	3	-496	0.048	-	-
Reagent	H_3PO_4	3	-1279	0.11	-	-
Thermodynamic parameters of the reaction	-	-	-1084.6	0.397	-1202.906	-2731.9899

The change of the standard Gibbs energy ΔG < 0. This means that the reaction (1) can take place at room temperature. The increase in the reaction mixture temperature will increase the rate of chemical reaction.We can assume the possible formation of polyphosphates in zeolite pores.

Conclusion

In this paper the statics and thermodynamics of ortophosphoric acid adsorption on natural zeolire are given. Taking into account the results of thermodynamic calculations, it was confirmed that the absorption of ortophosphoric acid occurs via the mechanism of polymolecular adsorption.

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Development of Energy-Efficient Shell and Tube Heat Exchangers for Use in Geothermal Heating Systems

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Abstract* – *The results of studies of the intensity of heat transfer using thin-walled corrugated tubes of various modifications for working on model coolants that have an increased density and viscosity (a highly mineralized medium with a salt content of 250 g/kg as the model coolants) are presented in the paper.

Keywords – heat exchanger, corrugated tubes, discrete turbulizers, highly mineralized media.

Introduction

Currently, low mineralized thermal waters are mainly used in geothermal heating systems. Low mineralized thermal waters do not need additional water treatment and the development of special equipment. However, the reserves of such waters are small and may soon be exhausted. There is a drop in production wells in most cases.

The large-scale use of medium potential geothermal energy is primarily associated with the development of mineralized geothermal waters, which constitute a large part of the existing reserves. However, the content of a significant amount of dissolved salts and gases in them causes their high corrosiveness and tendency to scaling. As a result, one of the main problems with the use of such quality water is the development of methods to fight corrosion and scaling.

Main Material

The main requirement for heat exchangers is a high heat transfer capacity and low loss in hydraulic resistance, and they must be compact and lightweight. It is necessary to take into account the properties of working media and the ability to work with polluted media, when solving standard heat engineering problems using heat exchangers. The cleaning of heat exchange equipment from contamination is the actual problem. Existing cleaning technologies are inextricably linked with labor costs, additional costs of fuel, chemical reagents, and environmental issues. To solve these controversial issues is possible only with the use of the latest developments and technologies that allow to obtain maximum heat exchange efficiency while reducing overall dimensions, as well as high reliability in operation and maintenance of heat exchangers.

Most of the existing heat exchange equipment does not take into account the properties of working medium, and therefore it is unstable. For example, plate heat exchangers are able to work exclusively with clean media, so one of the advantages of shell-and-tube heat exchangers is that they do not need a clean working media, and can work effectively with media that have a varied chemical composition and increased viscosity.

The problem of using highly mineralized media as a heat carrier is scaling on the heat exchange surface of the heat transfer wall, which increases the thermal resistance and reduces the heat transfer coefficient of the heat exchangers.

In the search for methods of intensification of heat exchange processes, studies of foreign and domestic scientists are constantly monitored. Currently, the passive methods of intensification of heat transfer and, in particular, the developed heat exchange surfaces are widely used. So far, no universal methods and criteria have been developed for evaluating the effectiveness of heat exchange surfaces. It is needed further study of thermal and hydrodynamic processes occurring in developed heat exchange surfaces in order to obtain generalized dependencies for calculating thermal and hydraulic characteristics and evaluating their effectiveness.

Choosing for practical application of heat transfer intensification method, it is necessary to take into account not only the efficiency of the surface itself, but also its manufacturability, the manufacturability of the apparatus, the strength requirements and the surface pollution.

Domestic industry produces flexible stainless corrugated tubes of small diameter. Such heat exchange surface is characterized by compactness, low specific cost, the ability to create complex heat exchange surfaces due to the “bend” of the heat exchange surface and the twist of the bundle of corrugated tubes. Corrugated tubes provide turbulence near the surface of the tube wall, thereby reducing the thickness of the thermal boundary layer. As a result, the mixing of the fluid near the tube wall is improved, due to the separation perturbations from the wall to the main flow, thus increasing the overall heat transfer coefficient in the heat exchange systems. Creating a self-oscillation mode of the heat exchange tubes during fluid movement prevents the formation of deposits on the walls of the tubes, thereby solving the actual problem of contamination of the heat exchange equipment.

The results of theoretical and experimental studies of the intensity of heat transfer using thin-walled corrugated tubes of various modifications to work on model heat transfer media with an increased density and viscosity (mineralized solution with a salt content of 250 g/kg as a model medium) are presented in the paper [1, 2]. Comparative analysis of operating modes of a heat exchanger with a corrugated inner tubes of various modifications and a heat exchanger with a smooth inner tubes when working on model coolants showed that, despite the increased density and viscosity, highly mineralized solution compared to water, corrugated tubes form an efficient turbulization of the near-wall layer and provide high heat transfer coefficients. On the basis of the obtained data, an effective heat exchanger is created (Fig. 1). The heat exchanger consist of thin-walled flexible stainless steel corrugated tubes as heat-exchanging elements, which are able to work with different chemical composition media and increased viscosity. This heat exchanger is designed to solve standard heat engineering problems taking into account the properties of working media.

Fig.1. Shell-and-tube heat exchanger with corrugated tubes

Conclusion

The use of flexible stainless corrugated tubes in heat exchangers allows to create high flow turbulence at relatively low coolant velocities, provides high heat transfer coefficients in the apparatus even when using highly mineralized and viscous media. The results of the study of an experimental sample of a tubular heat exchanger and the achieved values of the heat transfer coefficient (more than 3000 $W/m^2 \cdot K$ with a coolant mineralization of about 250 g/kg) illustrate the potential of the proposed approach and can be used to calculate and design heat exchangers intended for use in power engineering and geothermal power engineering.

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The Effect of Ultrasound on the Polymerization of Methacrylic Esters Compositions with Polyvinylpyrrolidone and Mineral Fillers

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Abstract* – The impact of ultrasound on the laws of the polymerization of methacrylic ester compositions with polyvinylpyrrolidone and mineral fillers has been investigated. The influence of ultrasound, the nature and amount of inorganic filler, the intensity of ultrasound on the rate of polymerization, the composition of the copolymers and the porosity of the composites has been established. It is confirmed that ultrasound significantly intensifies the polymerization and actively influences the formation of the composition of the copolymers.

Keywords – polyvinylpyrrolidone, ultrasound, mineral fillers, porous composites, filler, hydroxyapatite, osteoplastic materials.

Introduction

High adaptability to existing technologies, flexibility and efficiency, the possibility of using ultrasound (US) in a wide frequency range allows the use of ultrasonic technologies. Both basic and auxiliary methods that allow to intensify technological processes and significantly improve the quality characteristics of the received materials.

The purpose of the work is to investigate the effect of ultrasound on the polymerization of glycol methacrylate esters with polyvinylpyrrolidone (PVP) in the presence of mineral fillers, to determine the effect of the amount and nature of inorganic filler, PVP content and ultrasound intensity on the polymerization rate, composition of copolymers and porosity of composites.

Results and Discussion

Ultrasound was used to create active polymerization centers in viscous monomer-polymer compositions and to disperse the filler in the polymer composition and improve the uniformity of its distribution. For this purpose, the ultrasonic device "Wave" was used (the frequency of mechanical vibrations - 22 ± 1.65 kHz, the power control interval - 0-400 VA). Composites were filled with mineral fillers of various nature (hydroxyapatite, volostanit, montmorillonite, tricalcium phosphate).

It has been established that the compositions of (meth)acrylic esters of glycols with PVP under the action of ultrasound polymerize at high speed in heterogeneous conditions even without using traditional polymerization initiators at low temperatures. Homogeneous compositions polymerize much more slowly and subject to the presence of radical polymerization initiators in the reaction mixture.

The active influence of the nature and amount of the filler on the grafting parameters, the composition of copolymers and the properties of composites based on them has been established. Mineral fillers create a heterogeneous environment in the compositions, as a result of which, under the action of ultrasound, polymerization occurs very quickly with simultaneous foaming of the composition, which provides additional technological advantages in creating a technology for producing porous composites.

Depending on the nature of the mineral filler, the reaction of polymerization of compositions under the action of ultrasound, can occur both by the radical and ionic mechanisms. The participation of PVP in graft and block copolymerization reactions was confirmed by infrared spectroscopic studies. The main results of kinetic studies are given in the Table 1.

Table 1

The effect of ultrasound on the rate of polymerization (*T = 298 K, 120 VA*)

№	The composition of the polymer-monomer materials, mass.p			$V_p \cdot 10^2$	Maximum monomer conversion ,%	Time to reach to maximum conversion, s
	HEMA	PVP	filler			
1	100	0	0	0	–	–
2	70	30	0	2,2	90	190
3	70	30	70 HA	10,4/0,42	94	50/7500
4	70	30	100 HA	12,1	96	50
5	70	30	150 HA	17,5	97	45
6	70	30	70 WL	11,8	96	45
7	70	30	70 MMT	16,6	95	35

HA – hydroxyapatite, WL - wollastonite, MMT – montmorillonite.

- denominator without using ultrasound at 328 K.

The composites obtained under the action of ultrasound have a pronounced porous structure, which is confirmed by photographs taken using transmission electron microscopy. Under the action of ultrasound, the porous structure of the composites is formed, even without the use of special blowing agents. The basic properties of porous composites (total porosity, pore diameter, conditional density, compressive strength) are investigated in dependance on the composition of the original compositions, the nature and the amount of filler. With the same filler content in the case of using montmorillonite, the obtained composites are marked by the smallest average pore size. Composites with wollastonite have the largest pore diameter and low mechanical properties.

Conclusion

The expediency of using ultrasound for the formation of composites based on methacrylic ethers with PVP, filled with fine mineral fillers, has been confirmed. The use of ultrasound allows polymerization at room temperature and to achieve a high degree of monomer conversion to the polymer in a short time. This will significantly intensify the process of obtaining porous composites and increase its performance.

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Energy Effective Equipment for Polyextracts Producing

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Abstract* – *The results of modeling of the polyextracts obtaining process under electromagnetic field conditions are presented. The scheme of formation of traditional diffusion and additional hydrodynamic components from solid phase of raw materials is shown. The stages of solid phase and extactant interaction under electromagnetic field conditions are considered. The principal scheme of line of the polyextracts and their concentates production is presented.

Keywords – extraction, evaporation, drying, electromagnetic field, vacum, polyextracts.

Introduction

Extraction is a key process in many chemical, pharmaceutical and food industries. This process often determines the duration of the technological cycle, energy intensity and quality of the finished product. Traditionally, the process is based on the selective interaction of a specific target component of the solid phase and extractant. To obtain complex compositions - polyextracts, they use either a cascade of devices, in which the solid phase sequentially interacts with extractants of different nature, or with multiphase extractants. The search for new technical solutions in the problems of extraction is relevant.

Research Results

The authors created a fundamentally new equipment for extraction. The constructions are based on the principle of volume energy supply and hypothesis realization: "with certain combinations of the structure of the raw material and electromagnetic field parameters, initiation from the capillary-porous structure of the solid phase of a powerful mechanical flow, carrying with it a complex of target components of soluble and extractable extractant components, is possible" The devices implement a new effect, which the authors called "mechanodiffusion". If traditional extraction technologies provide only diffusional mass transfer from the solid phase, then the proposed constructions create conditions for the exit of additional vapor-liquid flows from the volume. The driving force of these flows is the pressure difference (Fig. 1). The condition for the functioning of such structures is the presence of polar molecules.

The raw material after preliminary machining is fed to a vacuum extractor of electrodynamic type (EDE). The sources of energy in the apparatus are microwave magnetrons. To stabilize the temperature regime during the processing of thermolabile raw materials, a refrigerator is installed in the device. At the end of the extraction process, the extract is fed to an evaporator (VMWA), and the solid phase is fed to a belt dryer bunker (BD).

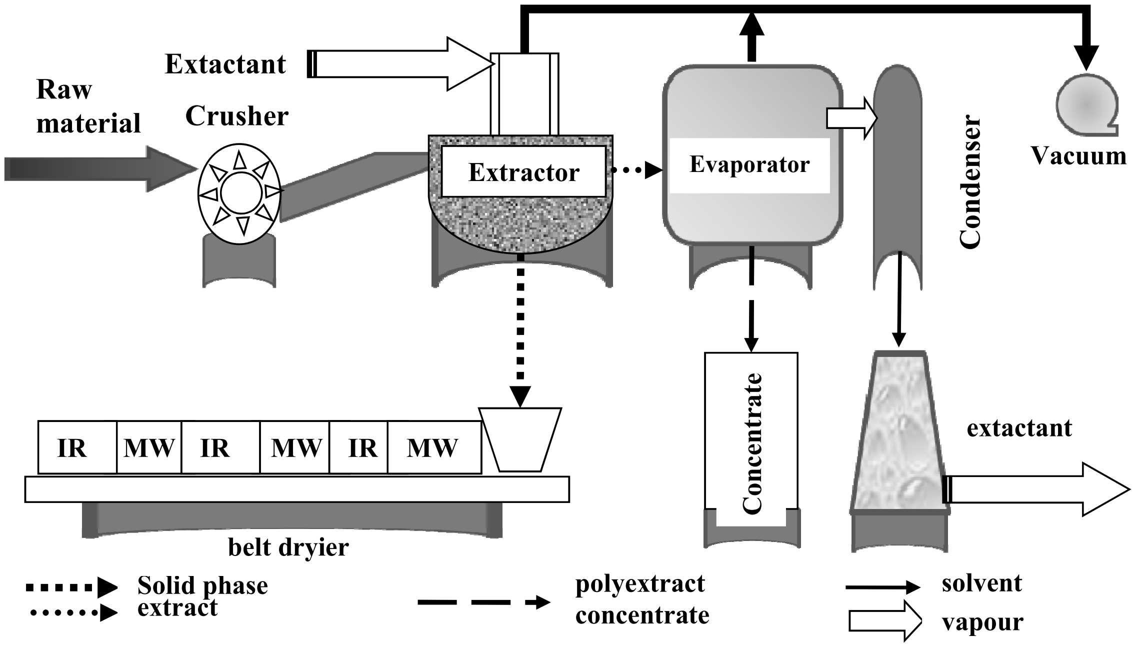

Fig.1. Raw material processing line with electrodynamic apparatus for extraction, drying and evaporation.

The solid phase on the tape moves sequentially through a cascade of cameras with microwave (MW) and infrared (IR) intensifiers. The task of MW generators is to deliver moisture from the volume of raw materials to the surface. The task of IR generators is to remove moisture from the surface.

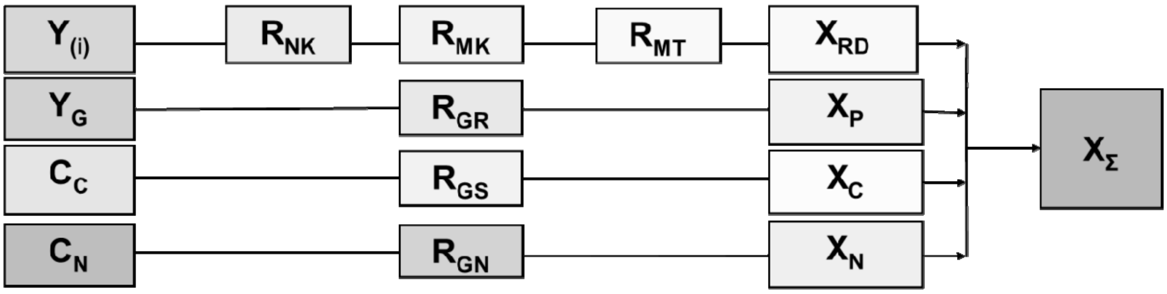

Fig.2. Equivalent electrodiffusion scheme of conjugate processes.

Here, Y (т) and YΓ – respectively, flowing in the solid phase and the boundary value of the concentration of soluble components; XΣ – the total value of all components transferred to the extract; CC and SN, respectively, concentrations in the solid phase of the poorly soluble and insoluble in the extractant components; XC and XH – the same, but in the extract. Based on the classical thermophysical mass transfer scheme [1], the diffusion transport mechanism from the fibrous structure to the flow corresponds only to the part of the circuit (fig. 2- 3). The successive chain of diffusion resistances consists of the sum: RHK (nanocapillaries), RMC (microcapillaries) and RMT (mass transfer).

The total flow of all components in the integral form is determined:

$$\Sigma M_I = (M_{P1} + M_{P2} + M_C + M_H)F^{-1} = \frac{Y - X_{РД}}{R_Д} + \rho\left[\frac{P_К - P_0}{R_{ГР}} + \frac{P_К - P_0}{R_{ГС}} + \frac{P_К - P_0}{R_{ГН}}\right] \quad (1)$$

The possible mechanisms of transport processes in the system "cell volume-shell-intercellular space-environment" are presented in Table 1.

Table 1

Mechanisms and stages of the transfer processes of components from plant raw materials in the gradientless supply of electromagnetic energy

Raw material elements	Mode and mechanism of the process	Processes stages
Intercellular space	Mass transfer during extraction due to diffusion mechanisms	1) Extraction of the extractant into the channels; 2) Diffusion of soluble substances in the cramped conditions of the capillary; 3) Convective diffusion from the interface into the medium
Intercellular space	Mass transfer of soluble and insoluble components from channels into the medium due to inertial forces	1) Formation of the center of vaporization; 2) Growth of pressure in the channel; 3) The release of components from the channels into the medium
Cell volume	Combined energy, filtration and diffusion effects on cell contents, mechanical action on the cell membrane	1) Formation of the center of vaporization; 2) The growth of pressure in the cell, and its volume; 3) Transition of components from the cell volume into the intercellular space
Cell sheath	Deformation of the cell membrane due to internal pressure forces	1) Increase in the degree of stress state of the cell membrane; 2) Increase in the diameters of the permeable channels of the membrane; 3) Rupture of the membrane

Conclusion

The use of address energy delivery technology allows to create principal new equipment for conducting of extraction and dehydration processes. The proposed construction of extractor makes it possible to obtain multicomponental solutions and polyextracts by the one extractant. The new construction of evaporator allows to thicken extracts up to 90 °brix. The proposed belt dryier is able to get dehydrated solid phase with low energy consumption.

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Corrosion Resistant Two-Layer Glass-Ceramic Coating

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Abstract* – *The composition of the soil glass coating of the Na_2O-SiO_2-P_2O_5-MoO_3 system has been developed. The minimum glass-forming temperature for the protective coating layer is determined. It has been established that the soil layer increases the adhesion of the coating to the metal substrate.

Keywords – solution technology, glass-ceramic coating, soil coating, glass-making solutions, adhesion.

Introduction

The using of inorganic coatings is effective for protecting metal parts and equipment from the effects of aggressive action of gases, solutions, melt and solids and also it increased their useful life. The glass-enamel coatings are particular importance and spread due to the unique combination of their mechanical strength, thermal and chemical resistance, lack of aging, surface smoothness and hygienic properties. In this regard, the development of warehouses of glass coatings for the protection of metal equipment from corrosion is a topical task today.

Research Results

The purpose of the work was developed a composition of corrosion-proof double-layer glass-ceramic coating with high adhesion to a metal substrate with using soluble technology.

The multicomponent silicate glass system of Na_2O-B_2O_3-TiO_2-SiO_2 with a refractory filler ZrO_2 was chosed to achieved the intended purpose as a corrosion-resistant layer. The temperature formation of a defect-free ceramic coating is 760 °C. However, the results of studies had showed that the resulting coating was characterized by low values of adhesion to the metal substrate (0.4 MPa).

In order to increase the adhesion of the glass-ceramic coating for the steel substrate were used a layer of soil, for receiving which, had selected a system based on phosphate glass. A characteristic feature of this system are elevated value of the temperature coefficient of linear expansion, high adhesion to the metal and low temperature of formation. The research has been established that these requirements correspond to the soil composition of the composition (% by weight): Na_2O – 36, SiO_2 – 45, P_2O_5 – 9, MoO_3 – 10. As the starting reactants have been used $Na_2MoO_4 \cdot 2H_2O$, $Na_2HPO_4 \cdot 12H_2O$, NaOH, H_3PO_4 and sodium fluoride with module 2. The above reagents were dissolved in water, based on their solubility and mixed in a certain stoichiometric relationship with the liquid glass. The obtained glass-making solution was applied to a heated metal substrate to 300 °C with subsequent melting in a gradient furnace at temperatures about 300-800 °C. As a result of heat treatment at 780 °C, the layer of soil firmly fixed on the surface of the metal was obtained. Adhesion of the soil layer to the metal surface is 3.4 MPa.

Conclusion

Thus, the two-layer corrosion-resistant glass-ceramic coating with high performance characteristics had obtained with using a solution technology at low energy and material costs during formation due to the consistent application of soil and protective layer.

Forced Modulation of Operating Conditions in Chromatographic Separation: Potential and Pitfalls

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Abstract* – *Efficiency of chromatographic separations can improved by modulating the operating variables, such as mobile phase composition and temperature, as well as column loading conditions. The potential of the modulating methods and troubleshooting related issues will be discussed.

Keywords – chromatographic separation, pitfalls, gradient mode, solvent gradient, temperature gradient.

Research Disscusion

Chromatographic processes in both laboratory and large-scale applications are often performed in gradient mode, whereby operating conditions are modulated during the course of separation to improve its effectiveness. In liquid chromatography the composition of mobile phase (solvent gradient) and temperature (temperature gradient) can be used as operating variables.

In solvent gradient mode the mobile phase composition is varied from low to high elution strength. It is realized by an abrupt or a continuous change in the concentration of the so-called modifier, i.e., solvent that is added to alter adsorption properties of feed components, or by modulation of pH or the content of inorganic salts in the mobile phase. The advantage of solvent gradients is the possibility of separating multicomponent mixtures of components differing markedly in the retention behavior, accelerating the separation speed and compressing band profiles. However, when the added gradient shape is wrongly chosen peak deformation occurs. Moreover, when the modifier is retained by the stationary phase over the gradient concentration range, the shape of the imposed gradient may also be deformed, which disturbs the retention behavior of eluting compounds and deteriorates the column performance. Such deformations may occur in the course of gradients of organic solvents as well as inorganic salts or pH.

Gradient mode can be also employed for loading the column, where different solvents are used for preparing the feed solution (strong solvent) and for the mobile phase (weak solvent). Strong solvents are employed to increase the column load with feed components exhibiting poor solubility in the mobile phase. Because the elution strength of the feed solvent and the mobile phase usually differs markedly, the presence of the feed solvent may alter the adsorption behavior of solutes and cause deformations of their bands.

Another process variable that can be modulated in the course of chromatographic elution is temperature. Temperature gradients modulate retention of compounds to be separated on temperature-sensitive chromatographic media. It can be used to replace solvent gradient and avoid problems with handling multicomponent mobile phases, or both gradients can be combined to improve separation efficiency. Uncontrolled temperature changes may however cause non-uniform distribution of temperature in radial and axial direction and departure of the temperature gradient and the corresponding peak shape from the desired form.

Because of the complexity of thermodynamic, kinetic, and hydrodynamic effects underlying gradient elution, selection of optimal conditions for the separation is often impossible without understanding the band migration phenomenon. As efficient tools for understanding band migration phenomena and process design equilibrium theory and detailed models of the column dynamics are available, which will be discussed and exemplified in the lecture.

The Metallized Polyethylene Granules as the Basis for Creating of Thermal Energy Storage System

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Abstract – The possibility of using the technology of metallization of granular polymeric raw materials for the production of an active substance in the development of thermal batteries has been considered. On the example of copper granules of polyethylene, an increase in the efficiency of a thermal battery due to the higher thermal conductivity of the active substance in comparison with non-metalized polyethylene granules has been shown.

Keywords – metallization, granules, polyethylene, energy storage, thermal conductivity.

Introduction

A characteristic feature of the energy sector of Ukraine is the dominant role of nuclear power plants in the production of electric energy. Manoeuvrable power of the nuclear power industry is insignificant and it is used to work in the basic mode. In view of the significant unevenness of daily consumption of electricity, there is a need for implemented of measures that will allow to equalize daily electricity consumption. The One of solutions is the implementation of the "night tariff", and with it the development of systems of electric power supply with the possibility of accumulation of excess heat. A thermal battery (TB), as a system that provides reversible processes for the accumulation, storage and return of thermal energy, can be proposed to optimize the production and consumption of heat energy.

Experimental

To obtain the active substance TB, the technology of metallization of granular polymeric raw material [1] was used, which provided the formation of a solid copper layer on polyethylene granules containing copper content of 3 to 15 wt. %. The research of the laboratory model of TB showed the increase in the maximum temperature that can be achieved on thermocouples placed at a distance of 13 and 25 mm from the surface of the heater. With copper content on PE granules 15 wt. % temperature was 172 and 142 °C, at a heater temperature of 350 °C, which is higher compared to unmetallized PE granules: 155 and 91 °C, respectively.

Conclusion

The obtained preliminary results of the research of the thermal battery model using copper granules polyethylene allow us to assert that they are promising and will be continued in the direction of establishing the optimal metal content as well as the size of the granules.

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Bacterial Cell Disruption by Process of Hydrodynamic Cavitation. Mechanisms and Application

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Abstract* – The article presents complete understanding of bacterial cell disruption process under hydrodynamical cavitation (HC) condition. Analysis of present literature has shown that the process of cavitation is widely used in the food, chemical, pharmaceutical, and biological industries and is effective from ecological and energy point of view. Novel studies presents mechanisms, which ascertain fact of complete or partially cell wall destruction, but not explain reasons of this. The article proposes mechanisms and their theoretical justification for the extraction and sterilization process, and the thermophysical parameters necessary for conducting a particular process are determined.

Keywords – hydrodynamic cavitation, disruption, cell wall, sterilization.

Introduction

Many scientific papers are devoted to the use of hydrodynamic cavitation in sterilization technologies. Researchers of cavitation effects on biological cells describe the high efficiency of HC treatment. The advantages of such processing are the reduction of the processing time, reduction of energy consumption and the amount of chemical reagents, environmental friendliness of the technology. The results of existing microscopic studies indicate that under HC conditions, the pasteurization or sterilization effect is provided by the destruction of the cell wall of microorganisms, as a result of the impact and shear mechanisms at the final stage of compression of the cavitation cluster [1, 3]. However, the detailing of these mechanisms at the micro level and the quantitative calculation of the force effect of cavitation on the cells were not carried out. The clear understanding of HC process are necessary for investigation the effects of cavitation on biological cells. The works [1, 2] describe the thermophysical foundations of the cavitation process, show methods for calculating hydrodynamic and thermodynamic parameters that cause the partial or complete suppression of microflora.

Analysis of the Cell Structure and the Mechanisms of its Destruction

Cytoplasm is contained inside the cell, which is separated from the surrounding fluid by a thin (8 ... 10 nm) semi-permeable plasma membrane with a pore diameter (ion channels) of 0.4 ... 0.5 nm. The osmotic pressure of the cytoplasm (0.3 ... 1.0 MPa) acts on the membrane surface inside. The cell membrane is surrounded by a thin and durable cell wall that prevents tearing and stretching of the plasma membrane. The pore size of the cell wall is 4 ... 5 nm, it is permeable to water, salts and low molecular weight compounds. The strength of the cell walls of microorganisms reaches 100 MPa, which is comparable to the tensile strength of some steel grades [4]. The role of cavitation mechanisms in the inactivation of bacterial cells is far from being studied. The death of microorganisms is associated with hydromechanical, thermal, chemical, electrical effects of cavitation or with the combined effect of these factors.

For analyzing the impact of shock pulses of pressure of a cavitation cluster we are assumed that the bacterial cell in the form of a sphere or a cylindrical rod is in equilibrium with a liquid medium with pressure =0,1 MPa. On the inner surface of the cell wall with thickness through the elastic semipermeable membrane adjacent to it osmotic pressure acts as a result, tensile stresses arise in the walls. Tangential magnitudes and normal stress in the bacterial bacillus cell wall is estimated using the formulas:

$$\sigma_t = p_c R_c / h \text{ and } \sigma_n = p_c R_c / 2h, \qquad (1)$$

and the normal tension in the spherical bacterial wall is as follows:

$$\sigma_n = p_c R_c / 2h \qquad (2)$$

where R_c – the radius of the cylindrical part of the bacteria, and in (2) – radius of the sphere.

Parameter p_c - pressure acting on the inner surface of the wall. For large values of the p_c tensile stress may exceed the tensile strength of the wall, which leads to its destruction. According to these formulas, the calculation of the strength of the wall of such microorganisms S. aureus, L. lactis, Lactobacillus, E. coli was carried out, which was 1.20 MPa, 2.67 MPa, 1.75 MPa and 0.8 MPa respectively.

With a sharp increase in pressure in the surrounding fluid ($p_l > p_{l0}$), the internal pressure on the cell wall decreases sharply, which leads to a weakening of the stresses acting in it. When $p_l > \pi$ the magnitude of tensile stresses in the cell $\sigma \rightarrow 0$. The excess pressure applied to the outer surface of the plasma membrane leads to compression of the cytoplasm and an increase in the internal pressure in it from π to $p_l = \pi + \Delta p$. As a result, the potential energy of the compressed cytoplasm increases, and after a sharp relief of external pressure , it is realized in the form of a shock effect on the inner surface of the cell wall and cell death.

Studies of the effects of shear stresses [4] showed that the shear rate required for the destruction of gram-positive bacteria in the form of a sphere, lie in the range of $8\cdot10^6\ldots9\cdot10^7$ s^{-1}, and for the destruction of gram-positive bacteria in the form of a stick, a shear rate of about $5\cdot10^3\ldots7\cdot10^5$ s^{-1}. As is well known, cavitation processes are characterized by the appearance of radial currents caused by the growth and collapse of cavitation bubbles, which also has a dynamic effect on bacterial cells.

Experimental

To confirm the validity of these mechanisms, experimental studies have been carried out on the suppression of the microflora of milk on equipment that implements a combination of hydrodynamic effects (cavitation, explosive boiling up) and thermal effects. In this technology, cavitation effects are implemented in the impeller of centrifugal pumps, which are used as product pumps for pumping a liquid product, and according to the technology conditions they work nominally in cavitation mode. Milk is consistently subjected to a double cavitation effect. The first stage of cavitation treatment occurs in the pump, which operates in the temperature range of 50 ... 60 °C. After leaving the pump, the milk undergoes heat treatment in a pasteurizer ($T_{l\max}$= 80 ... 95 °C). The second stage of cavitation treatment is carried out before leaving the apparatus in a centrifugal pump operating in the temperature range of 25 ... 30 ° C. The level of cavitation in each of the pumps, as shown below, depends on the temperature mode of treatment.

Results and Discussion

The total bacterial contamination decreases by more than two orders of magnitude after heating the milk from 4 °C to 50 ... 60 °C and cavitation treatment in the first pump. After heat treatment in a pasteurizer at T_l = 95 °C, the total bacterial contamination decreases even more than an order of magnitude. After passing through the zone of adiabatic boiling up and subsequent cavitation treatment in the second pump at T_l = 30 °C, seeding decreases by almost an order of magnitude. The number of bacteria S.aureus and E. coli fig. 1 (a, b) decreases to zero already at the first stages of processing, since they are characterized by low wall strength. There are practically no surviving cells of the gram-positive Lactobacillus in the samples taken at the exit from the apparatus, while their content in the samples taken after the pasteurizer is still quite high. Survived after processing cells L.lactis, with a stronger cell wall determine, mainly, the level of residual contamination of milk.

The obtained data indicate that a significant contribution to the inactivation of microorganisms makes cavitation created in centrifugal pumps. Most researchers are inclined to believe that the role of cavitation in the destruction of bacterial cells lies in the action of the shock and shear mechanisms at the final stage of compression of the cavitation cluster [1, 4].

Pressure pulses calculated according to the data of [5] calculated within the model (fig. 2), for different values of liquid temperature T_l, [1], emitted by a cavitation cluster in the pump impeller at the moment of bubble collapse. The amplitude of the pulses $p_{l\max}$ max decreases from 2.3 MPa to 1.2 MPa with increasing liquid temperature from 20 to 60 °C. The magnitude of the pressure pulses is insufficient to destroy the solid cell wall of bacteria L.lactis, which is consistent with the results of the experiment. At the same time, the obtained results show that the intensive suppression of the vital activity of Lactobacillus bacteria in the final stage of treatment at = 30 °C observed in the experiment can be explained by the action of cavitation in the second pump when the condition $p_{l\max} = p_{cr}$ is fulfilled.

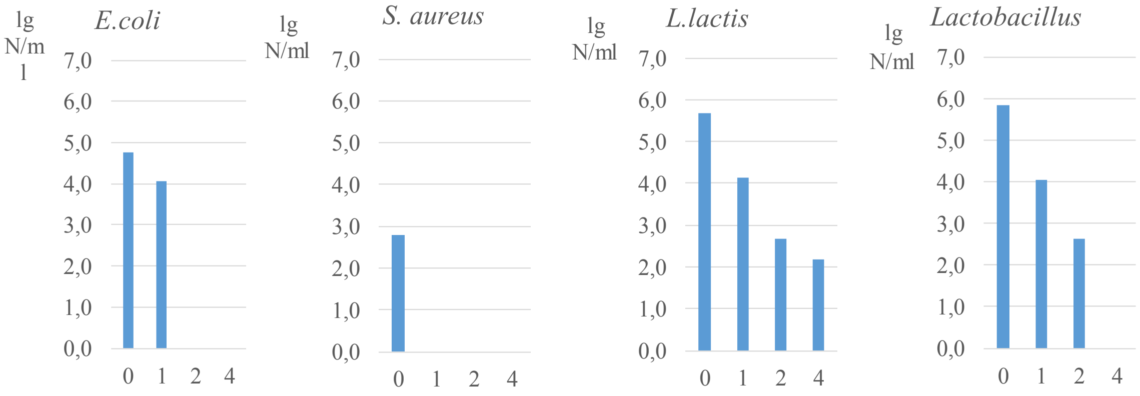

Fig. 1. Amount of bacterial cells at the stages of thermo-hydrodynamic treatment: 0 - initial sample; 1- first stage of the cavitation influence, 2 - thermal treatment; 3 – second stage of the cavitation influence.

The system of equations of the model of the dynamics of an ensemble of vapor bubbles is presented at the work [1], which makes it possible to calculate instantaneous values of pressure and velocity vector at local points inside the 3D cavitation cluster at all stages of its evolution. Using the model, one can estimate the level of shear stresses under various conditions of cluster formation and development. In fig. 3, a presents the calculated data on the change in the magnitude of the velocity in the XY plane passing through the center of the cluster in the X direction over a section of 0.3 mm in length for eight consecutive values of the Y coordinate with an interval of 10 μm. In fig. 3b for the same time point shows the change in the direction of the velocity vector at the same local points.

The presented data indicate a strong vorticity of microcurrents within the cluster. Calculations show that shear rates at local points of the cluster at the boundaries of the interaction of microflows are 10^5 ... 10^6 s^{-1}, which is comparable with the values of this parameter achieved in rotary apparatuses and in valve homogenizers.

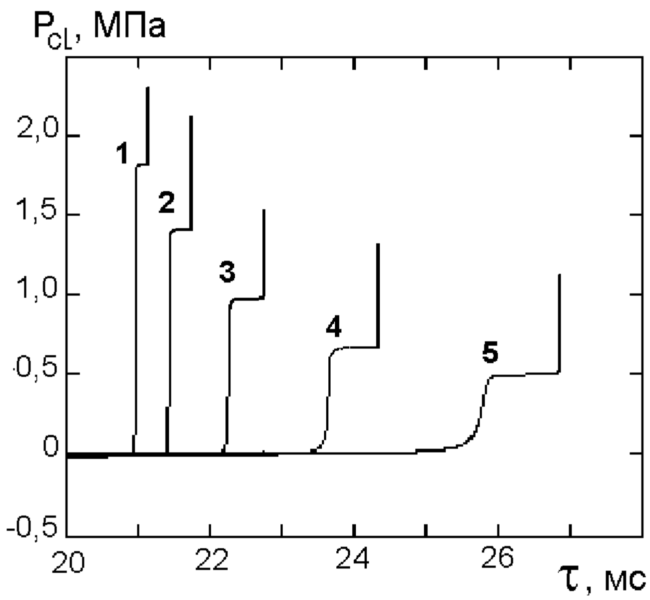

Fig. 2. The dependence of pressure in time in the volume of the cavitation cluster at different values of the temperature of the liquid : 1 - 20 °C; 2 - 30 °C; 3 - 40 °C; 4 - 50 °C; 5 - 60 °C. The pulses correspond to the moment of bubble collapse.

With regard to low-viscosity fluids (water, milk), this corresponds to shear stresses of the order of 0,001 ... 0,1 MPa.

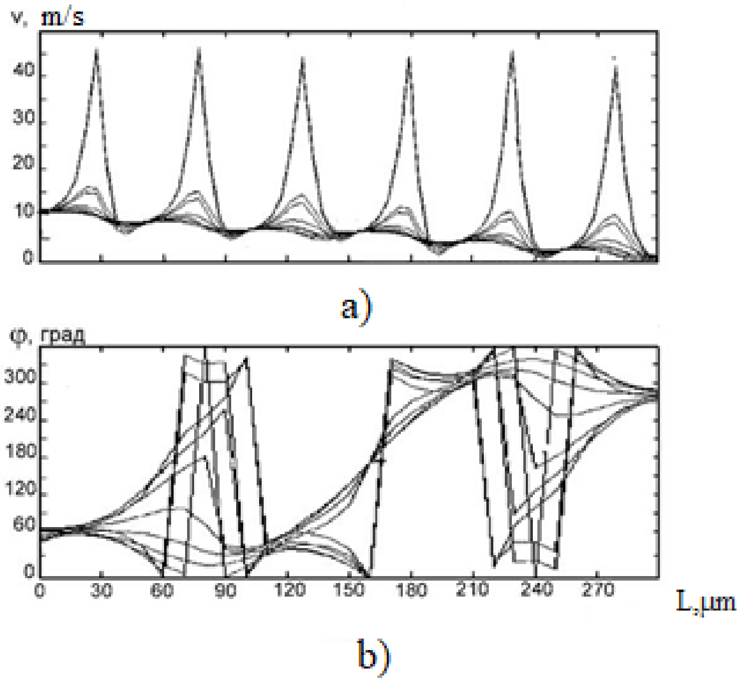

Fig. 3. a) - the change in the magnitude of the velocity vector along the X direction in the 3D cavitation cluster for eight consecutive values of the Y coordinate with an interval of 10 µm; b)- changing the direction of the velocity vector in the same X direction for the same Y coordinate values.

According to many researchers, shear stresses of this level can destroy the cell walls of even gram-positive bacteria [6]. The results we obtained are consistent with the results of the research of other authors. In [4], it is noted that the values of shear rates necessary for the destruction of cells of gram-positive bacteria in the form of a sphere are in the range of $3 \cdot 10^6$ ... $9 \cdot 10^7$ s^{-1}, and for the destruction of gram-positive bacteria in the form of a rod - in the range of 2

$\cdot 10^4 \ldots 7 \cdot 10^6$ s^{-1}. For the destruction of gram-negative rods, shear velocities of the order of $5 \cdot 10^3 \ldots 7 \cdot 10^5$ s^{-1} are sufficient.

Conclusion

This study shows that technologies based on the methods of HC can be applied to bacterial sononation of various media. The degree of suppression of microflora depends on the parameters of cavitation, which must be individually selected depending on the purpose of treatment. Low process temperature allows processing thermolabile raw materials. The significant contribution of cavitation to the suppression of undesirable microflora of milk allows to reduce the pasteurization temperature. The reduction of excessive thermal effects on the thermolabile product contributes to its quality indicators, as well as the energy efficiency of its processing.

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Influence of the Shear Flow Rate on the Effect of Water Purification During the Process of its Deferrization in a Rotor-Pulsating Apparatus

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***Abstract* – This paper presents the results of studies to determine the purification effect in the process of water deferrization in an aerator-oxidizer at different shear flow rates over a certain number of processing cycles.**

Keywords – deferrization, aerator-oxidizer, ejector, purification effect, shear flow rate.

Introduction

Aeration remains the most common method of natural waters deferrization. In addition, under the condition of intense aeration, the efficiency of other methods increases [1].

At the Institute of Engineering Thermophysics of the National Academy of Sciences of Ukraine, studies were conducted to the use of the rotor-pulsating apparatus as an aerators [2,3].

In the work [4] the results of research on the oxygen absorption rate in water solutions in the setup, consisting of an ejector unit and a disperser-mixer which is a rotor-pulsating apparatus are presented. The aim of the work was to evaluate the efficiency of the rotor-pulsating apparatus in the aeration of aqueous solutions by the method of chemical oxidation by air`s oxygen of sodium sulfide, which was a part of the model solution.

By comparing the efficiency of aeration of some setups with the studied sulfite method under the generalized criterion, it was determined that, with the disperser-mixer proposed in this study, the specific energy consumption per unit of dissolved oxygen was an order of magnitude higher than the pneumatic and mechanical aeration types found in the literature.

Materials and Methods

Studies to determine the purifying effect in the process of water deferrization were carried out on an aeration and oxidation setup with a rotor-pulsating apparatus as an aerator-oxidizer and an ejector installed in the suction nozzle of the rotor-pulsating apparatus. The scheme and principle of the setup is given in [5]. Table 1 shows energy and hydraulic characteristics of the setup.

Table 1

Energy and hydraulic characteristics of the setup

Shear flow rate, s^{-1}	$106 \cdot 10^3$ s^{-1}	$132 \cdot 10^3$ s^{-1}
Air water mixture flow, м^3/h	3.38	3.56
Air flow rate м^3/h	0.98	1.31
Pump head, MPa	0.04	0.07
Power consumption, kWh	1.62	2.35

Studies were carried out on model solutions at an initial iron (II) concentration of 3.5 mg/L during a certain number of processing cycles followed by filtration.

Results and Discussion

During the experiment, in the aerator-oxidizer , the shear flow rate, which is the product of the angular velocity of the rotor-pulsating unit on the inner diameter of the large rotor divided by the gap between the rotor and the stator, was changed.

To analyze the efficiency of the process, we selected the effect of water purification for one processing cycle, the value of which was calculated by the following equation:

$$E_{def} = \frac{C_0 - C}{C_0} \cdot 100\% \qquad (1)$$

where C_0 - initial total iron concentration total iron, mg/dm^3; C - total iron concentration after one processing cycle, mg/L.

Tables 2 and 3 show the purification effect during water processing in the aerator-oxidizer at a shear flow rate of $10^6 \cdot 10^3$ s^{-1} and $132 \cdot 10^3$ s^{-1}.

Table 2

The effect of water purification at the shear flow rate of $106 \cdot 10^3$ s^{-1}.

Number of processing cycles	Iron consentration, mg/L	Purification effect,%
0	3.50	67.14
1	1.15	47.82
2	0.60	48.30
3	0.37	30.00
4	0.30	24.00

Table 3

The effect of water purification at the shear flow rate of $132 \cdot 10^3$ s^{-1}.

Number of processing cycles	Iron consentration, mg/L	Purification effect,%
0	3.50	87.50
1	1.80	80.00
2	0.50	60.00
3	0.20	40.00
4	0.11	14.00

The data presented in tables 2 and 3 indicate that during the first processing cycle, the purification effect of in both cases is the highest compared to the subsequent cycles. So, with the shear flow rate of $10^6 \cdot 10^3$ s^{-1}, the purification effect is almost 70% at a concentration of Fe (II) ions of 3.5 mg/L and about 30% at a concentration of Fe(II) 0.5 mg /L. Increasing the shear flow rate of $132 \cdot 10^3$ s^{-1} leads to an increase in the purification effect of the first processing cycle up to 85% at the concentration of Fe (II) ions of 3.5 mg/L. During subsequent processing cycles, the concentration of Fe (II) ions decreases to 0.5 mg/L and the purification effect is reduced to 60%.

Conclusion

It is determined that the greatest effect of water purification in the aerator-oxidizer is observed after the first processing cycle and its value increases with increasing shear flow rate.

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Enzyme Complexes for Preparation of Spelt Wort in Alcohol Production

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Abstract* – *The effective complex of enzyme preparations for the spelt wort production was proposed: Amylex 5T (source of α-amylase), Diazyme SSF (source of glucoamylase), Laminex BG2 (source of cellulase) and Alphalase AFP (source of protease) for the hydrolysis of biopolymers spelt grains.

Keywords – enzymes, spelta, wort, yeast, mash.

Introduction

Starchy and sugar-based raw materials are used mainly for the production of food alcohol. Research on the selection of alternative raw materials is directed at those plants that contain starch and sugars. Spelt (Triticum spelta L.) is a kind of wheat that has a film grain and a scalene rod. Its cultivation does not require significant agronomic costs, since the cereal has drought and cold resistance and mature very quickly. Spelt is an environmentally friendly crop [1].

It is known [2] that the content of proteins in the spelt is 28% higher than in wheat, fats - in 1,6 times, and mineral substances - by 22%. According to the results of research [2], spelt grains contain more soluble fractions of food fibers, vitamins and minerals. Carbohydrate-based polymers (starch, cellulose) are used as carbon source during the microbiological formation of ethanol and the generation of biomass of yeast But these carbohydrates can be used by microorganisms only after hydrolysis of them to mono- and disaccharides.

Proteins in the spelt after enzymatic hydrolysis to amino acids become a valuable source of not only nitrogen, but also carbon for the life of yeast. Given the presence of these acids in the wort for the formation of biomass yeast consumes less sugar, and more - for the production of alcohol. Hydrolysis of pectin substances is not important in the production of alcohol, but during the preparation stage, their hydrolysis is desirable due to the fact that it reduces the viscosity of the medium. Cellulose of raw materials under the influence of cellulolytic enzymes is partially hydrolyzed to glucose, which increases the yield of alcohol and reduce the viscosity of intermediate products of alcohol production. All these processes are carried out with the participation of hydrolytic enzymes that catalyze the hydrolysis of starch, cellulose, protein and pectin substances.

Consequently, the task of finding effective enzyme preparations complexes for the preparation of spelt wort with the properties necessary for the alcohol production is actual and of practical importance.

Materials and Methods

The subjects of the research were: commercial enzymes («Danisco», Denmark), spelt wheat (Triticum spelta L.) of the variety «Zorya Ukrainy», were obtained from Ukrainian Scientific Institute of Plant Breeding (Kyiv) and dry alcoholic yeast Thermosacc DRY. The technological parameters of spelt grain are: humidity 10,5%, starch 44,0%, debris with grain impurities 1,5% and garbage impurities – 1,0%, grinding size - 92% of the throughput through a sieve with a diameter of holes 1 mm. Fermentation of spelt wort was carried out in flasks at 33 ± 10C for 72 hours. In the work, the research methods adopted in the alcohol industry were used. Evolved CO2 was controlled by gravimetric method. In fermented wash the content of ethanol was determined by distillation method.

Results and Discussion

The choice of enzyme preparations was due to peculiarities of grain raw materials and their chemical composition. The lower content of starch in grain grains of the special varieties "Zorya Ukraina" in comparison with wheat increases the content of non-starched polysaccharides. Therefore, in order to effectively transform starch, as well as other components of grain raw materials into digestible sugars and components for the nutrition of yeast, complexes of enzyme preparations based on α-amylase, glucoamylase, cellulase and proteases were proposed. For the decomposition of non-starched polysaccharides contained in the filamentous part of the grain spelled, a proposed Laminex BG2 AF, capable of maintaining activity at 60 - 700C and recommended by the manufacturer to make it during the preparation of dough. Alphalase AFP with a temperature optimum of 500C is proposed for the decomposition of protein substances (table 1).

Thermo-enzymatic treatment of milled grain with water was carried out at a temperature of 76 ± 10C for 2,5 hours, and saccharification - 30 min at 55-60 0C. The ratio of water to ground grain was 3 : 1. The efficiency of the enzyme complexes was determined depending on the rheological properties of the wort, such as the viscosity of the wort, indicating the efficacy of starch hydrolysis, the content of dry matter and the pH of the wort.

The results of studies on preparation of spelt wort using enzyme complexes (table) indicate that the introduction of cellulases and proteases leads to a decrease in viscosity of the wort and an increase in its concentration.

Table 1

Influence of complexes of enzyme preparations on indicators of spelt wort

Wort indicators	Complexes of enzyme preparations		
	Amylex 5T Diazyme SSF (control)	Amylex 5T Diazyme SSF Laminex BG2	Amylex 5T Diazyme SSF Alphalase AFP
Concentration of wort, %	16,2	16,7	16,5
Viscosity of the wort, Па·с	0,025	0,021	0,022
pH	5,9	5,9	5,7

Investigations of the spelt wort fermentation have shown that in the case of using amylolytic enzyme complexes with Laminex BG2 and Alphalase AFP, the mass of CO2, isolated during fermentation, increased by 2-4% compared with control. The content of alcohol in the bar, where the wort was received from Laminex BG2, was the maximum, and Alphalase AFP - the minimum.

Conclusion

Thus, among the investigated enzyme preparations for obtaining spelt wort in alcohol technology, the most effective was the complex on the basis of Amylex 5T, Diazyme SSF and Laminex BG2.

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Microwave Vacuum Extraction for Rosehips Polyextracts

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***Abstract* – Extraction in microwave field in vacuum is investigated in paper. Decrease in pressure and influence of microwaves on intensification of extraction of water- and liposoluble components. Use of water extractant instead of two-phase solvent systems simplifies technological process for production of polyextracts.**

Keywords – extraction, microwave assisted extraction, vacum, polyextracts, carotolin, rose hips.

Introduction

Rosehips are valuable raw materials for the production of phytopreparations and health food products. 100 grams of ripe cinnamon rose (Rosa cinnamomea L.) hip fruits contains about 2400 mg of vitamin C and carotenoids, causing bright coloration. Today, modern technologies of rosehips processing are divided into several basic stages, which include water extraction of fruits for preparation of ascorbic acid products in the Hezenko diffusers, and extraction with organic solvents of rosehip seeds and skin to obtain carotenoid preparations (carotolin) and rose oil (vitamin E). To extract liposoluble carotenoids organic solvents are used. Technology of obtaining polystracts with the two-phase systems of extractants, proposed by Kogan G.Ya., allowed to receive a convenient medical form combining water-soluble and liposoluble components [2].

The school of microwave extraction is developing in the Odessa National Academy of Food Technologies scientific school by professor O. Burdo`s group [3]. Barodiffusion effect occurring during impact of microwave field is investigated. Intensification of the process is achieved by boiling extractant in the capillaries of plant material, which forming steam bubbles, pushing the flow of components to the extract. Combined with the soluble components, water-insoluble components can also pass into the extract, for example: carotenoids. Consequently, there is a possibility of obtaining polystracts in devices with water solvent.

Research Results

For the experimental researches hip fruits of cinnamon rose (Rosa cinnamomea L.), produced by "Lubnifarm" company, with humidity of 15% are selected. Extraction carried out with water solvent (distilled water). The temperature was determined by the GM320 radiation pyrometer. The measuring range is 0 ... 330 ° C, with an error of ± 1.5 ° C. Measurement accuracy (scale interval) is 0.1 ° C. Amperage, voltage and field intensity indicators were determined using the KSP-50 measuring complex. Digital portable refractometer HI 96801, “Hanna Instruments”, were used to determine concentration of the extract. Measuring range: 0 ... 85 ° brix. Accuracy: ± 0.2 ° brix. To determine the amount of vitamin C in the extract, the Thilmans titration method were used.

Extraction is carried out in a dilution installation. Main components of the extractor are: magnetron, extraction chamber, condenser, water cooler, vacuum pump.

Before the experiment rarefaction is formed in the extraction chamber with a vacuum pump. During the experiment, pressure in the extraction chamber was stabilized by adjusting power of the supplied electromagnetic energy and the heat removal system. Reverse fridge is provided for condensing evaporated solvent. The temperature regime in vacuum microwave extractor is regulated by the water cooling system. The water cooler consists of refrigerator, circulating pump and thermostat.

Vacuum control in the system is provided by an exemplary vacuum gauge. Supply of the electromagnetic energy is carried out by the power electronics unit at the command of control unit, which contains a timer and a power regulator. Water cooler consists of steam-compressor refrigeration machine, tank with cooling water, water temperature regulator and circulation pump, which provides the supply of cold water to the condenser.

During the experiment, magnetron power and concentration of the extract changed. Mass of rosehips for whole series of experiments was 100 g. Ratio of solid phase and extractant is 1: 4. Pressure in the extraction chamber was maintained in the range of 20 ... 40 kPa (Fig. 1). On the basis of experimental data, we obtained the coefficient of mass transfer during extraction according to classical equation (1) [3].

$$\beta_e = \frac{V_e \cdot 100}{F_k \cdot (X_b - X)} \quad (1)$$

where β_e – effective coefficient of mass transfer, V_e – volume of extract, F_k – phase contact area, X and X_b – current and equilibrium concentration of the extract.

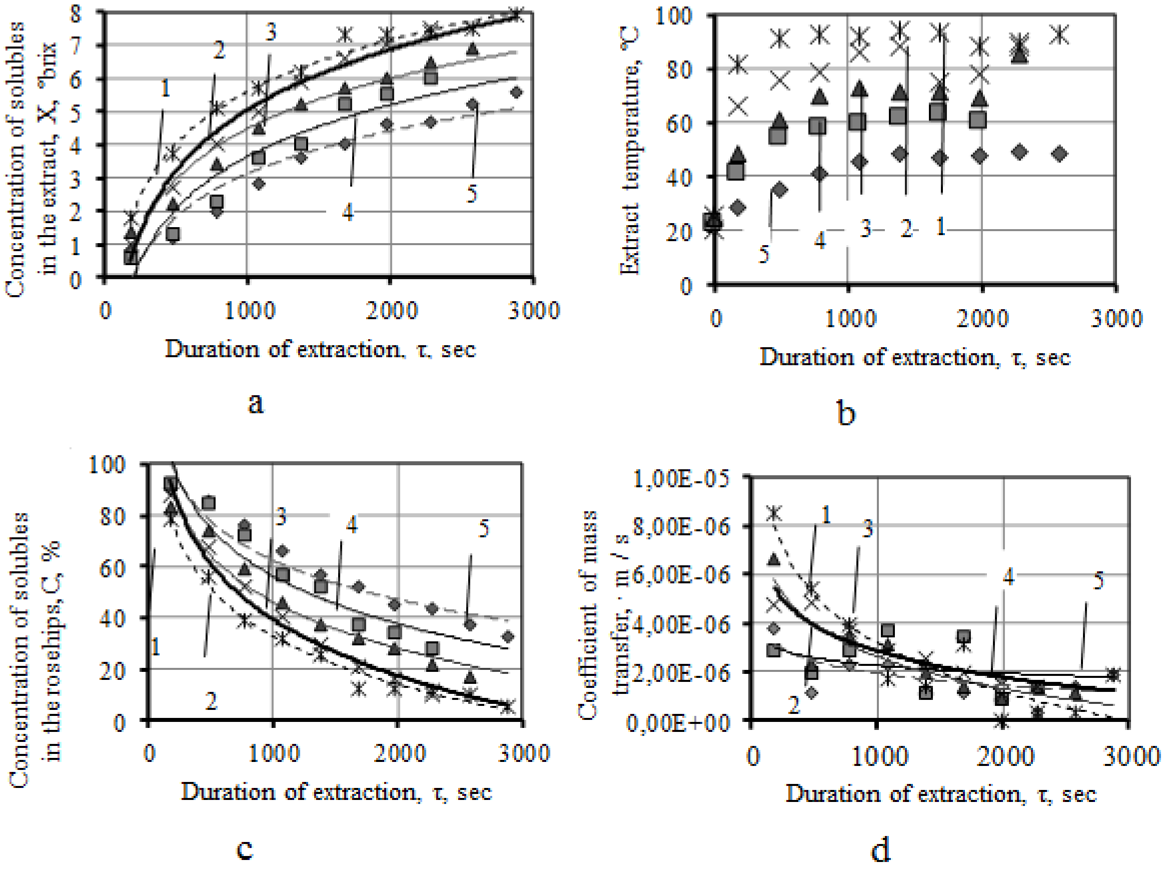

Fig.1 The kinetics of extraction in the VME (a), change in temperature of the extract (b), concentration of solubles in the raw material (c), and mass transfer coefficient (d) at different intensity of the microwave field: 1 –1024 W; 2 – 682 W; 3 – 512 W; 4 – 273 W; 5 – 136 W.

Extract obtained at temperatures lower than 60 ° C (1, 2 fig. 2), according to literature data, should retain more vitamin C, which is destroyed at higher temperatures. Content of vitamin C in the extract, obtained in microwave extractor compared with the one obtained in thermostat at temperature of about 40 ° C determined by titration method (Thilmans method). Results are presented in Table 1.

Table 1

Analysis results of ascorbic acid content in rosehips extracts

Sample	Concentration of dissolved solids, %	Content of vitamin C, mg / 100 cm^3	Relative content of vitamin C,%
Vacuum microwave extractor	4,2	430…550	10,2…13
Thermostat	4,8	310…380	6,45…7,9

Results of the experiment confirms high yield of vitamin C. In addition, content of carotenoids in the extracts were determined. This time, three samples was compared: sample obtained in thermostat, sample obtained in microwave extractor without using vacuum and sample obtained in microwave extractor under conditions of dilution. Results are presented in Table 2.

Table 2

Analysis results of carotenoid content in rosehips extracts

Indicator	Thermostat	Microwave Extractor	Vacuum microwave extractor
Concentration of dissolved solids, %	4,1	4,8	5,2
Beta-carotene, mg/100 cm^3	4,120…4,848	3,946…4,455	5,824…6,420

Results of the analysis demonstrate an increase of carotenoids yield using microwave vacuum extractor. According to the results, we can say that exactly pressure reduction has significant effect on output of carotenoids. Special conditions for reducing the viscosity and density of the extractant in conjunction with the directed action of microwave radiation contribute to intensification of the extraction of carotenoids.

Conclusion

Using of microwave effects with the system vacuuming, allowed to obtain an increased yield of not only water soluble but also oil soluble solids. The polyextract obtained with the aqueous solvent in one device should lower the price and simplify polyextract production technology.

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Studying on Liquid Phase Cyclohexane Oxidation Enhanced by Oxalic Acid: Pertinent Response by Long-Lasting Challenge

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Abstract* – *A new effective protocol for oxidation of cyclohexane in acetonitrile at 40 °C and atmospheric pressure into cyclohexanol, cyclohexanone and cyclohexylhydroperoxide using H2O2 as sustainable oxidant, vanadyl(IV)-acetylacetonate as starting catalyst, oxalic acid and glyoxal as activating additives is presented with some reaction mechanism proposals.

Keywords – mild oxidation, cyclohexane, vanadyl(IV)-acetylacetonate, H2O2, oxalic acid, glyoxal, process activators, mechanism.

Introduction

Despite the extensive efforts aim to elaborate of new effective and energy-spared protocol for the cyclohexane oxidation the denoted problem remains one among the biggest challenges of contemporary chemistry. It refer to the extended application of oxidized products, i.e. cyclohexanol, cyclohexanone and cyclohexylhydroperoxide as precursors in artificial fibers industry (Nylon 6 and 6,6). Indeed, these products are used to manufacture as much as 2.3×10^6 T adipic acid and 4.4×10^6 T of ε-caprolactam per year [1]. On the other hand, what is even more important, study by activation the extraordinary strong C—H bonds of C6H12 (BDE = 98 kcal mol^{-1}) would result in new fundamental knowledge be useful for elaboration the modern methods of others industrially-meaningful substrates functionalization. The actual study reports that the $VO(acac)_2$ (1) catalyzed cyclohexane oxidation by H_2O_2 at mild conditions is notably improved by using both glyoxal and it oxidized descendant oxalic acid (3). The putative mechanism the denoted additives influence is elucidated by GLC, UV-Vis, CV, EPR, ESI-MS.

Kinetics and Mechanism of C_6H_{12} Oxidation in Presence of Glyoxal and Oxalic Acid

In the absence of 2, the reaction of C_6H_{12} with H_2O_2 (1 equiv.by substrate) at 40 °C requires at least $(0.3 \div 0.6) \times 10^{-3}$ M of **1** to generate the detectable amounts of products – $C_6H_{11}OH$, $C_6H_{10}O$ and $C_6H_{11}OOH$ (Fig. 1). Below of this range the yield of aimed products was ignorable (curve 1, Fig. 1) and the level of H_2O_2 utilization (ΔH_2O_2) and it effectiveness (Eff_{H2O2}) was <1% and >90%, respectively (Table 1). The addition of **2** into the reaction mixture contained even 0.06 mM of **1** resulted in a four-fold increasing of cyclohexane conversion (even in respect to the 10 times higher catalyst concentration of **2**-free experiment) concomitant with the Eff_{H2O2} growing (entries 2 and 7, Table 1). Simultaneous decreasing the catalyst and substrate initial load (Table 1, entries 4 and 8) lead to enhancing the conversion, turnover number (TON), and process efficiency from 5% (entry 4) to 30% (entry 8) and and Eff_{H2O2} from 8% to 16%, respectively. Due to the instrumental analysis the initial **1** as well as the originated in situ $VO(oxalate)_2$ (Scheme 1, Fig. 2, 3) can interact with H_2O_2 produce the $VO(\eta\text{-}O)_2$–based species.

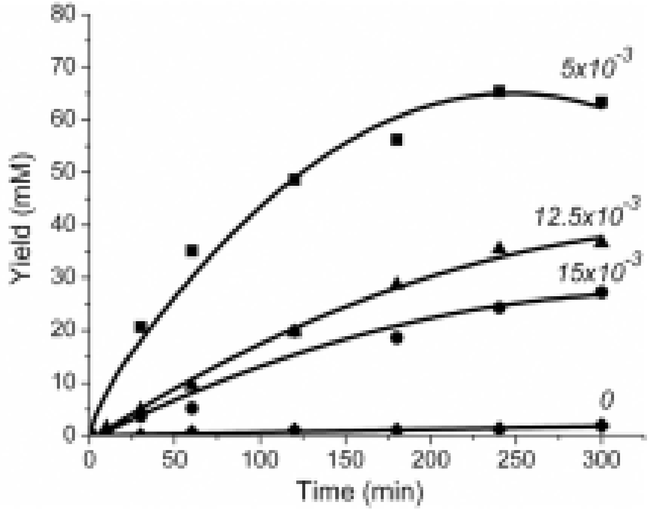
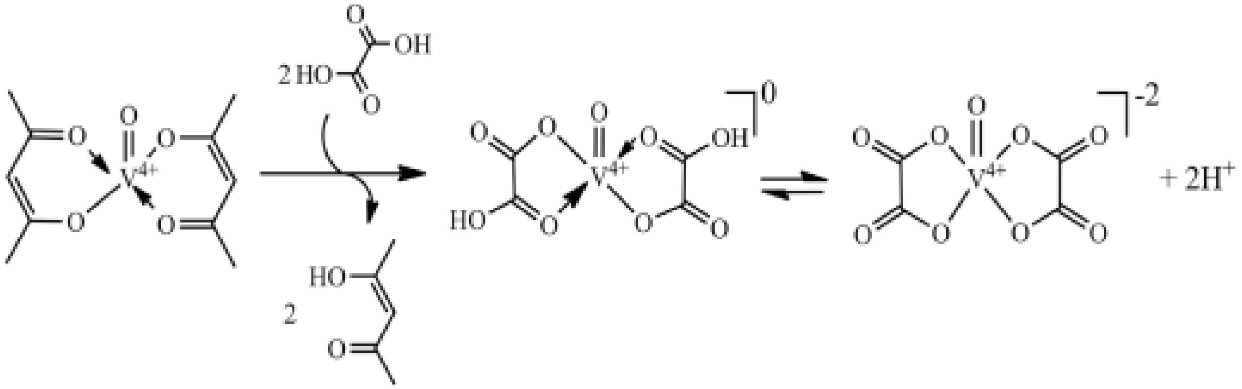


Fig. 1. Kinetics of sum products accumulation. Concentration of 2 is given in M above of each curve.



Scheme 1. The plausible structures of 1+2 interaction.

Table 1

The effect of 2 additives in 1-catalyzed cyclohexane oxidation.[a]

Entry	1	2	ΔC_6H_{12}	Selectivity, mol%			TON	ΔH_2O_2[b],	*Eff*$_{H2O2}$[c],
	×10^3, M		%	$C_6H_{11}OH$	$C_6H_{10}O$	$C_6H_{11}OOH$		%	%
1	0.06	-	<0.1	-	-	-	-	<1	>90
2	0.6	-	1.2	33	62	5	23	48	4.2
3	0.6	1.0	1.7	1	8	91	51	52	6.5
4	0.6	15	5.3	48	7	45	169	96	8.4
5	0.6	50	7.6	43	13	44	253	90	13.2
6	0.6	150	5.2	47	10	43	173	80	9.9
7	0.06	50	5.1	23	25	43	1516	25	32.4
8[d]	0.06	15	30	22	44	34	944	34	15.7
9[e]	0.06	30	0.2	29	29	42	56	5	6.8

[a] *$[C_6H_{12}]_0 = [H_2O_2]_0 = 1.8$ M; $[VO(acac)_2]_0 = 0.06\times10^{-3}$ M. MeCN, 40°C, 5 h. (For all catalytic tests, the products selectivity was above 90%).* [b] *Amount of H_2O_2 consumed.* [c] *Eff$_{H2O2}$ is the ratio of stoichiometric (by products yield) amount of H_2O_2 divided by the H_2O_2 consumed.* [d] *$[C_6H_{12}]_0 = 0.18$ M.* [e] *Acetic acid has been used instead of **2**. The ΔC_6H_{12} (substrate conversion) values match well with the products yield due to the almost 100% process selectivity.*

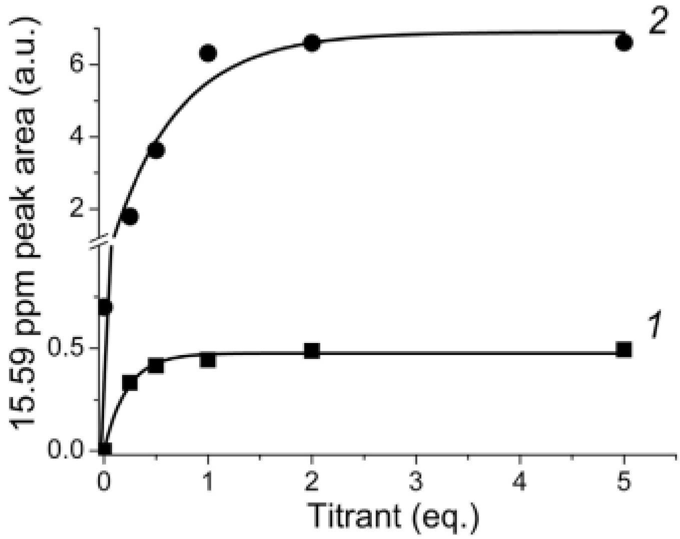


Fig. 2. Kinetics of enol OH peak (15.59 ppm) growing during of 1 (1.5×10^{-3} M) solution titration by H_2O_2 (1) and 2 (2), CD_3CN, 20 °C

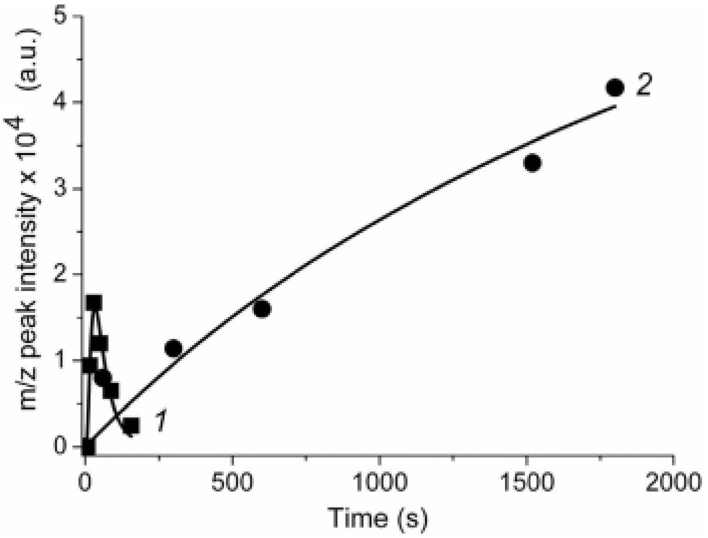


Fig. 3. Time-traces of $[VO(\eta\text{-}O)_2(acac)]^+$, m/z 198.981 (1) and $[VO(\eta\text{-}O)_2(oxalate)]^-$, m/z 186.908 (2) species accumulation.

Conclusion

Privilege formation of $VO(\eta\text{-}O)_2$ species in 1 + 2 oxidation is responsible for the revealed effect.

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Solubilization of Bifonazole in the Presence of Carboxymethylated-β-Cyclodextrin

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Abstract – ***Recently, many technological methods of enhancing the solubility and dissolution characteristics of poorly water soluble drugs have been reported in the literature. Cyclodextrins are able to form water-soluble non-covalent inclusion complexes with many poorly soluble lipophilic drugs. The purpose of this study is to evaluate the possibility of interaction of the antifungal drug Bifonazole (BFZ) through complexation with carboxymethylated-β-cyclodextrin (KM-β-CD). Based on the data obtained, we can conclude that the presence of KM-β-CD improves solubilization of BFZ more than 50 times.***

Keywords – cyclodextrins, solubility, poorly-water soluble drugs, bifonazole

Introduction

Currently, many technological approaches of enhancing the solubility and dissolution characteristics of poorly water soluble drugs have been reviewed in the literature. However, conventional methods used to prepare these systems suffer from serious limitations on their applicability in the market, often involving physical instabilities of the solid dispersions on storage, problems of grinding or difficulties in removing the toxic organic solvent [1]. The therapeutic effectiveness of a drug depends on its bioavailability and ultimately on the solubility of the drug molecule. Usually, only solubilized molecules can be absorbed by the cellular membrane to reach the specific site of drug action. So, now much attention is paid to the ability of cyclodextrins (CD) to form inclusion complexes with various organic substrates. Cyclodextrins are able to form water-soluble non-covalent inclusion complexes with many poorly soluble lipophilic drugs of proper size and polarity, leading to changes in their physicochemical and biopharmaceutical properties, which enhance their solubility, dissolution rate, chemical stability and bioavailability and reduce their side effects and toxicity. Cyclodextrins are also able to form non-inclusion complexes, aggregates and micelle-like structures, which also effectively solubilize poorly-water soluble drugs [2, 3].

Results and Discussion

Bifonazole (BFZ) ((RS)-1-[phenyl(4-phenylphenyl)methyl]-1H-imidazole) (Fig. 1) is a substituted imidazole antifungal agent that is structurally related to other drugs from the azole group. It possesses a broad spectrum of activity in vitro against dermatophytes, molds, yeasts, dimorphic fungi, and some Gram-positive bacteria [4]. It has a double mechanism of action as it works by preventing the 14-α-demethylation of 24-methylene-dihydrolanosterol, consequently preventing the formation of the cellular membrane by inhibiting the production of ergosterol, and also causes direct damage to the membrane [5]. It also shows an anti-inflammatory effect on erythema caused by histamine [6, 7].

Due to the imidazole cycle, BFZ is a basic compound (pKa 9.30), and due to the presence of the aromatic rings it is a lipophilic substance (log P 4.77) which is almost insoluble in water. BFZ has a water solubility of 0.7 μg/ml at 25°C [8].

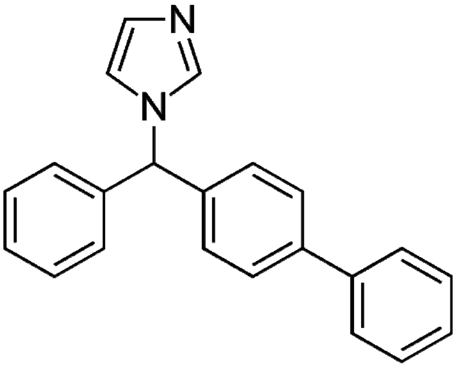

Fig. 1. Constitutional formula of BFZ

The purpose of this study is to evaluate the possibility of interaction of the antifungal drug BFZ through complexation with carboxymethylated-β-cyclodextrin (KM-β-CD).

So, we investigated the solubilization process for slightly soluble BFZ in the presence of KM-β-CD in comparison with other derivatives of cyclodextrin, like (2-Hydroxypropyl)-β-cyclodextrin (HP-β-CD), Methyl-β-cyclodextrin (β-CD-Met) and derivative of starch - carboxymethylated-starch (KM-Str.) by using method of UV-spectroscopy. Application of β-CD's derivatives and KM-Str. leads to improved solubilization of BFZ (Fig. 2). Based on these data, we can conclude that involving of β-CD and starch derivatives improves solubilization of BFZ nearly in 6-12 times. The best dissolution of the drug can be seen, while using KM-β-CD, in this case the solubility of BFZ is increased more than 50 times.

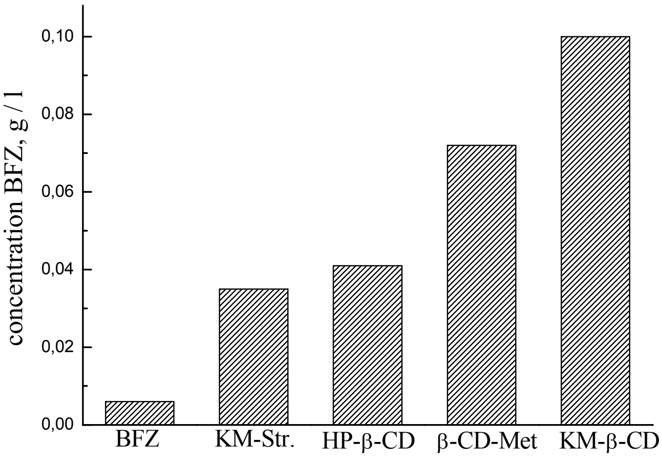

Fig. 2. Solubilization of BFZ

Conclusion

The obtained result can be explained by the double effect of the KM-β-CD: the presence of a hydrophobic cavity and active substitutes, which, apparently, participate in the protonation of the molecule BFZ. Thus, KM-β-CD significantly improves solubilization of BFZ, while the derivatives of β-CD and KM-Str. are less effective than KM-β-CD.

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Synthesis and Properties of the Glass R_2O-SiO_2-Nb_2O_5 System

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Abstract* – *Articles with the modification of traditional glass ionomer cement with niobium oxide have been analyzed. Ostend work results with modifications glass Nb_2O_5. Described is a test of the samples obtained. Conclusions are made regarding the influence of niobium oxide on the R_2O-SiO_2-Nb_2O_5 system.

Keywords – glass ionomer cement, modification of glass, sol-gel technology.

Review of Literary Sources

The influence of many oxides on the properties of glass is well-known. Most of them have been already investigated, which allows to analytically calculate the required property by the rules of additivity.

In our work we consider a niobium-containing glass, information on which is substantially limited.

Existing data from a number of authors indicate a significant influence of Nb2O5 on density, crystallization, refractive index of glass and, which is essential, on its biocompatibility. Based on niobium-containing glass, optical lenses are obtained, lately, niobium oxide has become a component of glass to obtain glass-ionomer cements for dentistry [1].

Influence of Niobium Oxide in the R_2O-SiO_2-Nb_2O_5 System

In this work, glass of the model system R_2O(Na_2O, K_2O)-SiO_2-Nb_2O_5 was investigated. The content of Nb_2O_5 was varied within the range of 18-25 mass %. Glass was melted from chemically pure materials at a temperature of 950°C. The obtained glass qualitatively melted without visible defects.

For all glass samples, density, water resistance, microhardness, and thermal coefficient of linear expansion(TCLE) were determined. It was established that with an increase of Nb_2O_5 in the content from 20% to 27%, the microhardness increases by 800 MPa.

Important are the results of determining the TCLE from a practical point of view. So, for glass containing Nb_2O_5 27 mass %, TCLE in the range of 20-300^{0}C is $178\cdot10^{-7}$ deg^{-1}, and with a content of 22 mass % it is $191\cdot10^{-7}$ deg^{-1}. This indicates a more compacted structure of glass with the applying of Nb_2O_5.

As for water resistance, it is fairly low for all glass samples. However, applying of Nb_2O_5 instead of alkaline oxides increases this parameter significantly.

Conclusion

A radical step in the matter of the synthesis of glass in this system will be sol-gel technology, the basis of which is currently being tested.

It is quite obvious that glass for glass-ionomer cements with high rates requires further modification of its composition.

Modeling of the Saturation Reactor in the Production of Pumpkin Candied Fruits

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Abstract* – *With the help of the universal simulation program ChemCad, an isothermal saturation reactor for sugar pumpkin particles was modeled, which operates under the constant concentration of sucrose in syrup and simultaneously increases the concentration of sucrose in candied fruits. Concentration of sucrose and the level of liquid in the reactor is not changed.

Keywords – saturation reactor, bubble, isothermal, mixing mode, simulation, candied fruit.

Introduction

The production of candied fruits is a priority development area of the food industry. The basic process in candied fruits production is diffusion of sugar syrup into vegetable raw material. ChemCad's universal simulator allows you to simulate the process of saturation of pumpkin fruit with sugar. The simulation results allow the implementation of a technological process with minimal energy consumption and maximum preservation of nutrients in the finished product, in which the only preservative is sugar.

Methods

The object of the research was particles of identical sizes of cubic shape (10 mm wide) from the pumpkin fruits of the "Stofunvotka Vassma" kind grown in the western regions of Ukraine. Pumpkin particles were saturated with sugar in syrup with sugar initial concentration of 70 wt.% using the installation.

With the help of the universal simulation program ChemCad, an isothermal saturation reactor for sugar pumpkin particles was modeled, which operates under the constant concentration of sucrose in syrup and simultaneously increases the concentration of sucrose in candied fruits (Fig.1).

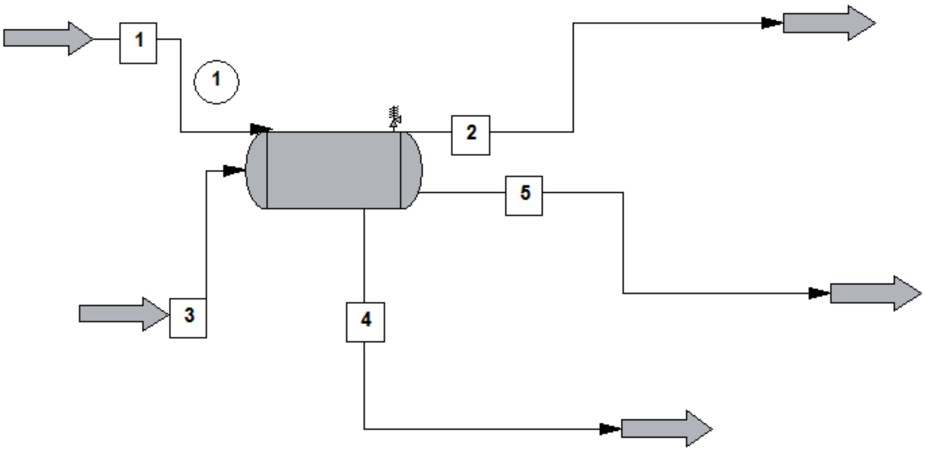

Fig.1. Model Dynamic vessel ChemCad for steady state
1 – feed stream (syrup); 2 – product stream (vapor); 3 – feed stream (pumpkin cubes of 10x10x10 mm size); 4 – product stream (syrup); 5 – product stream (candied fruit)

Such a process was modeled by stationary with intense mixing, operating in isothermal mode and in which amount of evaporated water compensates for the amount of water extracted from candied fruit.

Results and Discussion

For simulation, it was necessary to pre-analyze the mathematical description of the conditions for the implementation of the isothermal regime, to develop a mathematical support for the design of the reactor.

For simulation, it was necessary to pre-analyze the mathematical description of the conditions for the implementation of the isothermal regime, to develop a mathematical support for the design of the reactor to include:

- determination of the constant concentration of sugar in vaporized syrup at the end of the process, the flow of solution and vapor;
- duration of sucrose saturation under stationary conditions;
- definition of reactor design characteristics, diameter, height and height of the liquid.

Numerical simulation values, graphical (Fig.2, 3) and computational relationships are obtained, the result is analyzed.

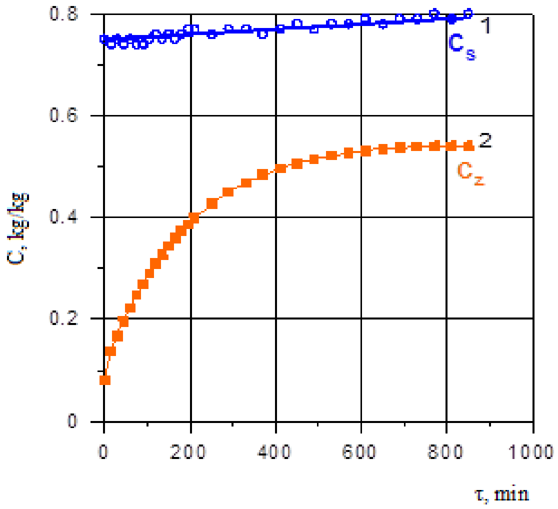

Fig. 2. Dependence of changes in sucrose concentration in syrup (curve 1) and candied fruits (curve 2) in time

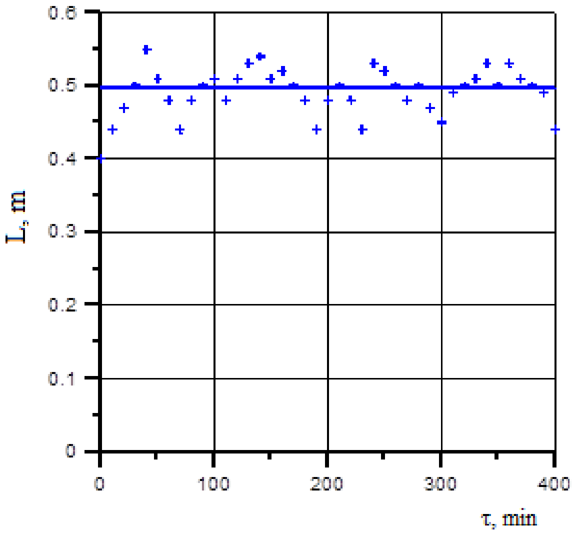

Fig. 3. Dynamics of change in fluid level in time

It is evident from Fig. 2, 3 that concentration of sucrose and the level of liquid in the reactor is not changed.

Conclusion

It is proved that the process of saturation of succulents with sugar in the steady state is advisable, in terms of preservation of organoleptic properties, optimum saturation of candied fruit, which will retain its properties and molds for a long time.

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Granulation Characteristics Study of Silicate Mass Charge Mixtures

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Abstract* – *The conditions and parameters of granulation of powdered silicate materials are considered in this work. The method of determining the strength of granular materials is proposed.

Keywords – polymineral clay, granulation, granulated glass-ceramic material, speed-range mode, optimal rotational frequency, strength.

Introduction

The development of new materials of different nature with stable operational properties involves the manufacture of products of various shapes and types on their basis. One of these materials is foam glass, which is characterized by reliable performance indicators and is made in the form of blocks and friable granules. The granular foam glass can be used as a friable heat-insulating filler of building technical constructions and in industry. Raw materials for the production of such products are broken glass, a foam generator of diverse nature, and a wide range of adhesives of diverse nature [1].

Results and Discussion

The compilations of this material, developed by us, are made from the charge compositions of the fracture system of glass-zeolite-containing component-clay [2,3]. The role and content of such components and their influence on the process of material polishing are studied in detail [4].

However, the issue of granulation of these materials requires further study. The granulation was carried out using a laboratory drum granulator with an inner diameter 500 and a length of 450 mm.

It has been established that the optimal rotational frequency was chosen based on the condition of material granulation due to its rolling in the second quadrant while rotating the drum counterclockwise, equals to [rpm]:

$$n = \frac{8 \div 14}{\sqrt{r}} \qquad (1)$$

where, r - radius of the interior of the granulator, m.

It has been established that the productivity and granulometric composition of the product depend on the charge, the fineness of its grinding and humidity.

The comparative strength of the granulate is proposed to be evaluated according to the intensity of the abrasion of dried granules when they are rotated in a laboratory ball mill for weight loss on a control sieve. The duration of the process is correlated with the conditions of their correction in a rotating kiln.

It has been established that the local highly plastic clay of the Yavoriv deposit in the amount of 15-25 % by weight promotes the process of granulation and increase the strength of the semi-finished product.

Conclusion

Thus, in the course of the work, the technological parameters of granulation of the developed charge mixtures were established, and a method for monitoring the strength characteristics of the granulate has been suggested.

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Investigation the Kinetics of the Process of destruction organic Contaminations Wastewater Production Margarine

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Abstract* – *The kinetics of the cavitational wastewater treatment process of the production of magragin from organic contaminants in the atmosphere of gases of different nature has been investigated. The comparative characteristics effective constants of the rates of destruction of organic substances and the coefficients of approximation are given.

Keywords – cavitation, wastewater, kinetics, effective constants of the rates.

Introduction

The wastewater of the fat and oil industry has a wide range of pollutants, therefore the way of its neutralization and the choice of processing method should ensure their complete disposal. The diverse nature and concentration of the pollutant in sewage in many cases do not allow to achieve the required quality of treatment by traditional methods [1]. In this case, technologies that use physical and chemical phenomena can be promising for the purification of natural water and sewage. One of the promising ways to improve water purification technologies is the use of cavitation phenomena. Cavitation technologies are environmentally friendly ways of improving the efficiency of technological processes of water purification [2]. The cost and efficiency of the cavitational water treatment process depends on the degree of their pollution, technologies and equipment which are used for their treatment.

Results and Discussion

The object of the study was wastewater of the JSC “Lviv Fat and oil plant”, a branch of margarine. Output values of chemical oxygen demand (COD) are in the range (705-1450) mgO2/dm^3. Studying the kinetics of the process of destruction of organic compounds, the data of the curves are rectified in half-logarithmic coordinates ln(COD/COD$_0$)=f(t), which suggests that this process can be described by the kinetic equation of the first order, and the tangent angle tg α = -k .

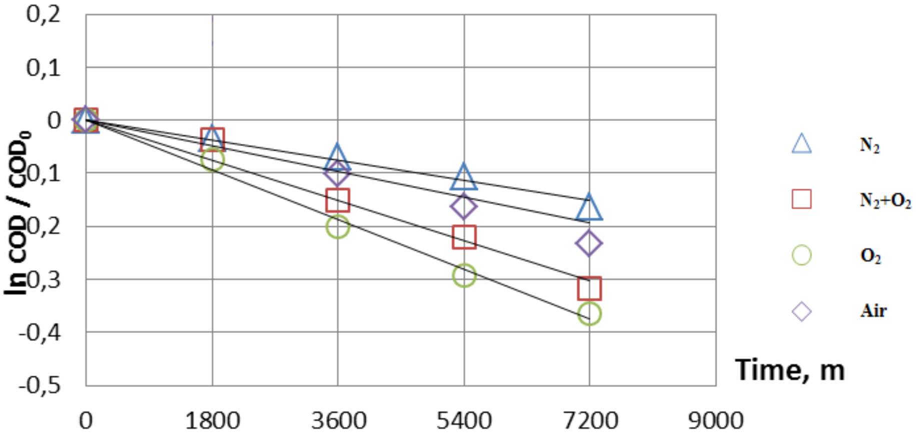

Fig. 1. Semi-logarithmic dependence of the ratio of COD / COD$_0$ of wastewater JSC “Lviv Fat and oil plant”of from time under different process conditions

At the action of the studied gases alone Fig. 1, the lowest result is achieved with nitrogen bubbling, the effective constants of the rates is 0.2 * 10^{-4} m^{-1}. Investigating the influence of the air, it was established that during its bubbling the effective constants of the rates is 0.3 * 10^{-4} m^{-1}. A little bit better result when giving a mixture of nitrogen and oxygen gases in the ratio of 1: 1, the effective constants of the rates is of 0.4 * 10^{-4} m^{-1}. The highest purifying effect is achieved with oxygen bubbling, the effective rate constant for water purification is 0,5*10^{-4} m^{-1}.

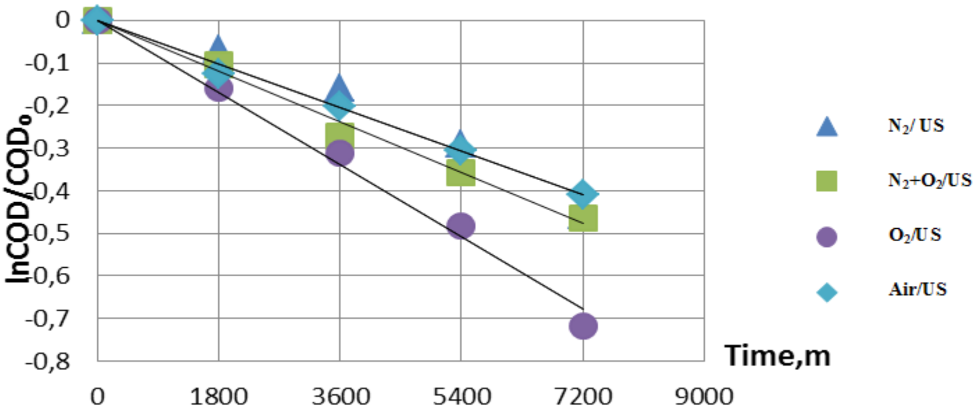

Fig. 2. Semi-logarithmic dependence of the ratio COD / COD0 of wastewater of the JSC "Lviv Fat and oil plant" from time in the presence of ultrasound under different process conditions

Bubbling the gases with different nature with ultrasonic fluctuations substantially improves the purification of investigated sewage, fig. 2. The greatest purification effect is obtained by oxygen bubbling in the US field, the effective rate constant for water purification is 0.9 * 10^{-4} m^{-1}. In the common action of the ultrasound with a mixture of gases of nitrogen and oxygen in the ratio 1: 1, the effective rate constant decreased to 0, 7 * 10^{-4} m^{-1}. When using air from US and nitrogen from US, we observe similar values of the effective rate constant - 0.6 * 10^{-4} m^{-1}.

Therefore, as we can see from Table 1, the obtained values of the effective constants of the rate of destruction of organic compounds in sewage under cavitation conditions are 1.75-3 times higher compared with the action of the gases itself.

Table 1

Comparative characteristic of effective constants of the rates of the process of cleaning wastewater of production margarine from organic contaminants in presence of gases of different nature

Conditions of the process	k*10^4, m^{-1}		R	
	Without US	With US	Without US	With US
N_2	0,2	0,6	0,955	0,984
O_2	0,5	0,9	0,990	0,991
N_2+O_2	0,4	0,7	0,974	0,989
Air	0,3	0,6	0,502	0,994

Conclusion

It was investigated that the cavitational process of wastewater treatment from organic contaminants, regardless of the nature of the bubbled gas, can be described by applying the kinetic equation of the first order, the highest purification effect is obtained with the common action of oxygen and ultrasound in cavitation conditions.

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Structure and Antimicrobic Properties of Nanocomposites Based on Anionic β-Cyclodextrin, Chitosan and Silver Nanoparticles

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Abstract* – *Structural organization and antimicrobial properties of nanocomposites based on chitosan, anionic β-cyclodextrin (β-CD) and Ag nanoparticles, being formed by the chemical reduction method from interpolyelectrolyte–metal complexes (IMC) chitosan–Ag*$^+$*– anionic β-CD have been investigated. It is defined that chemical reduction of Ag*$^+$ *ions by* $NaBH_4$ *in the interpolyelectrolyte complex results to formation silver-containing nanocomposites. The antimicrobial investigation of the elaborated nanocomposites revealed they possess a high antimicrobial activity against S. aureus and E. coli strains.

Keywords – interpolyelectrolyte complexes; interpolyelectrolyte–metal complexes; silver-containing nanocomposite; structure; antimicrobial activity.

Introduction

Nanoparticles of metals, such as copper, silver, zinc are in the focus of the researchers involved into development of effective antimicrobial agents due to their biocidal activity and high stability in extremal conditions.

Results and Discussion

To obtain the interpolyelectrolyte complex (IPEC), chitosan–anionic β-CD; the interpolyelectrolyte–metal complex (IMC), chitosan–Ag$^+$–anionic β-CD; and nanocomposites of IPEC–Ag the following reagents were used: cationic polyelectrolyte chitosan, anionic functionalized β-CD, silver (I) nitrate ($AgNO_3$).

IPEC samples were formed via mixing of 5% aqueous solutions of chitosan and anionic β-CD taken at a molar ratio of 1:1, at $T = 20 \pm 2$ °C. IPEC as films were prepared via pouring onto PTFE plates and drying up to constant masses at the same temperature. Dry IPEC films were washed in distilled water up to neutrality and dried repeatedly at 20 °C up to constant masses.

IMC samples were prepared via immersion of IPEC films into an aqueous solution of $AgNO_3$ with a concentration of 0.1 mol/L at $T = 20 \pm 2$ °C for 24 h. The colorless IPEC films became dark red.

The chemical reduction of Ag$^+$ ions in the IMC’s was conducted with $NaBH_4$ (a molar ratio of $[BH_4^-] : [Ag^+] = 2.0$) in an alkaline medium (pH 10.8) in a solvent mixture of water–isopropanol (4 : 1 vol %) at $T = 20 \pm 2$ °C for 3 h (until the release of gaseous bubbles ceased). The concentration of $NaBH_4$ in the aqueous alcohol solution was 0.1 mol/L.

As a result of the reduction IMC films changed color from red to metallic.

After the chemical reduction of the Ag+ ions in the IMC with the use of sodium borohydride (a molar ratio of $[BH_4^-] : [Ag^+] = 2.0$) nanocomposite based on the IPEC and Ag were prepared. In the diffractogram IPEC–Ag nanocomposite (curve 2) two intense maxima at 2θm = 38.2° and 43.8 are fixed, corresponding to the crystallographic plan of the face-centered cubic lattice of silver with (111) and (200) indexes respectively, confirming presence of metal silver in the polymeric system.

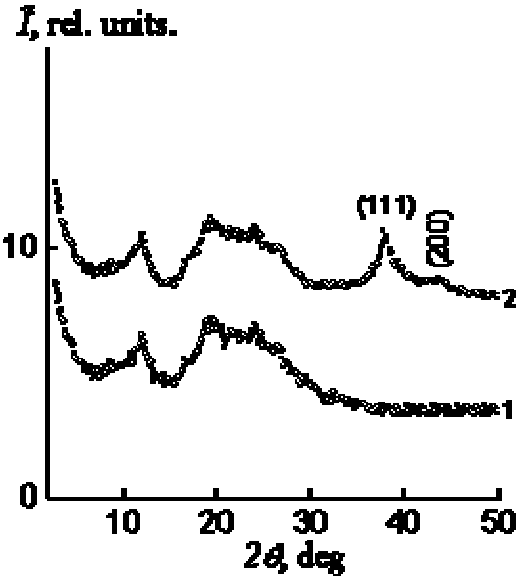

Fig. 1. Wide-angle X-ray diffractograms of (1) the IPEC; (2) the IPEC–Ag nanocomposites obtained via the chemical reduction of Ag^+ ions in the IMC at molar ratios of $BH_4^- : Ag^+ = 2$.

IPEC–Ag nanocomposites which created by chemical reduction of Ag^+ ions in IMC are found out to demonstrate highest antimicrobial activity against S. *aureus* and *E. coli* strains. After incubation proceeds for 24 hours at 37 °C one can observe a clear zone around the films' contours, thus confirming inhibition of bacteria growth. The growth inhibition's zone diameter for *E. coli* are 14.0 mm and 18.0 mm, correspondingly (table 1).

Table 1

Antimicrobial activity of the IPEC–Ag nanocomposites, prepared via the thermo and chemical reduction of Ag^+ ions in the IMC

The method of obtaining nanocomposite films	Diameter of inhibition zone, mm	
	Staphylococcus aureus	*Escherichia coli*
chemical reduction	IPEC–Ag 18.0±1.2	IPEC–Ag 14.0±1.2
control sample	IPEC 0	IPEC 0

Conclusion

Active growth of the test bacteria and absence of growth inhibition have been observed in the test specimens (polymer film without nanoparticles).

The Formation of Composite Film Hydrogel Membranes with Polyamide Layer

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Abstract* – *The composite hydrogel membranes on the basis of 2-hydroxyethylmethacrylate (HEMA) and polyvinylpyrrolidone (PVP) copolymers modified by a thin layer of PA-6/PVP mixture by the diffusion deposition from the solution were synthesized. The influence of the surface adsorption of PA-6/PVP mixture on the physical and mechanical properties of the synthesized films has been investigated.

Keywords – membrane, hydrogel, 2-hydroxyethylmethacrylate, polyvinylpyrrolidone, polyamide-6, surface adsorption.

Introduction

Polymer hydrogels, which are close to biological cells in their physical state, have proven to be effective in medicine and pharmacy. However, in practice the wide usage of hydrogel products is limited by their low mechanical strength, even though generally the application of hydrogels has a great potential . Recently, the interest to the polymer hydrogel materials, that have high mechanical strength in a hydrated state along with the hydrophilic and diffusion-transport properties, has increased.

The forming of composite hydrogel materials as coatings or multilayer films is carried out in order to improve the strength of the films, reduce their thickness, obtain a defect-free surface layer, create films of complex configuration and special properties. The processing of composite films focuses on the ensuring the necessary interlayer adhesion during combin of polymer film materials.

Results and Discussion

The composite polymer membranes are obtained by their surface modification with the thin layer of another polymer. The method is based on applying the polymer solution on the surface of the semi-permeable membrane substrate. As a result of solution diffusion into the surface layer, deposition of the polymer modifier occurs.

The aliphatic polyamides based solutions are promising for polymer hydrogels modification. The obtained films are hydrophilic with improved mechanical strength.

Monomer-polymer compositions were dissolved in the aqueous medium to form hydrogel film membranes. The polimerization was performed with the potassium persulfate initiation. Obtained hydrogel films were rinsed in the distilled water for 24 hours to completely remove unreacted monomer and stored in the hydrated state.

The hydrogel films were modified by the thin layer of solution consisted of PA-6/PVP, formic acid and water. One-sided coating of the thin polyamide polymer layer on the hydrogel film surface was achieved as a result of its contact with the hydrogel sample surface for a defined period of time - 1÷10 min, with further solvent evaporation under 75-80 oC for 30 minutes. Obtained composite hydrogel films were rinsed with water to complete removal of the solvent. In current study the films in the hydrated state were used.

Conclusion

The hydrogel membranes based on copolymers of 2-hydroxyethyl methacrylate and PVP, reinforced by the thin films as a result of PA-6/PVP polymer mixtures deposition from the solution, were synthesized. The dependence of their physical and mechanical properties on the surface adsorption was investigated. It was shown that the surface adsorption can be regulated by changing the hydrogel composition and the modifying polymer mixture as well as the holding time of hydrogel membrane in the modifying solution.

Vibro-Activeted Lime as a Regulator of Concrete Hardening

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***Abstract* – In order to increase the strength of the cement stone, an additive of vibro-activated lime is proposed. It is established that the maximum increase in compressive strength is achieved within the limits of 35-40%.**

Keywords – lime, cement, compressive strength, vibro-activation, additive, dispersion.

Research Results

In the technology of obtaining concrete products the actual task is to increase their strength through the introduction of special chemical applications. Particularly widespread use was made of salts of alkaline and alkaline earth metals formed with strong acids ($CaCl_2$, Na_2SO_4 and others), which are injected up to 2% of the weight of cement directly during mixing the raw material mixture with water. However, along with the positive effect of increasing the strength of hardened products in the process of their operation, it is also possible to form the salt outlets on the surface and reduce their corrosion resistance.

It is also known that the increase in strength is facilitated by the small supplement of quenched lime diluted with water breeding. The use of quenched lime prevents the formation of salt outlets and reduces the corrosion resistance of products, but this supplement gives a slight increase in firmness, which does not exceed 5%. A promising direction is the use of the supplement of quenched lime, which was subjected to previous vibration activation.

Vibro-activated lime is characterized with a much higher dispersion in comparison to the usual quench, resulting in a higher specific surface, and hence reactivity. Vibro-activation of quenched lime was carried out on an experimental laboratory vibration plant, designed on the basis of a vibration bunker, for 10-60 minutes. As the results of research showed most intensively, the process of dispersion occurs in the first 20-30 minutes of treatment, and then slowed down due to inverse aggregation of particles and their adhesion on the working surfaces of the plant [1].

It is also found out that the introduction of activated lime application of optimum dispersion parameters in the amount of 2% of the weight of cement increases the brand strength of the cement stone by 35-40%. In addition, the use of the supplement of vibration activated lime increases the plasticity of the prepared concrete mix.

Conclusion

The conducted studies have shown that along with the existing methods of activation of concrete hardening processes, this method is promising and at the same time technological, which at low cost allows to effectively influence the processes of hardening and significantly increases the quality of finished products.

Tempered Glass Obtained by Water Cooling

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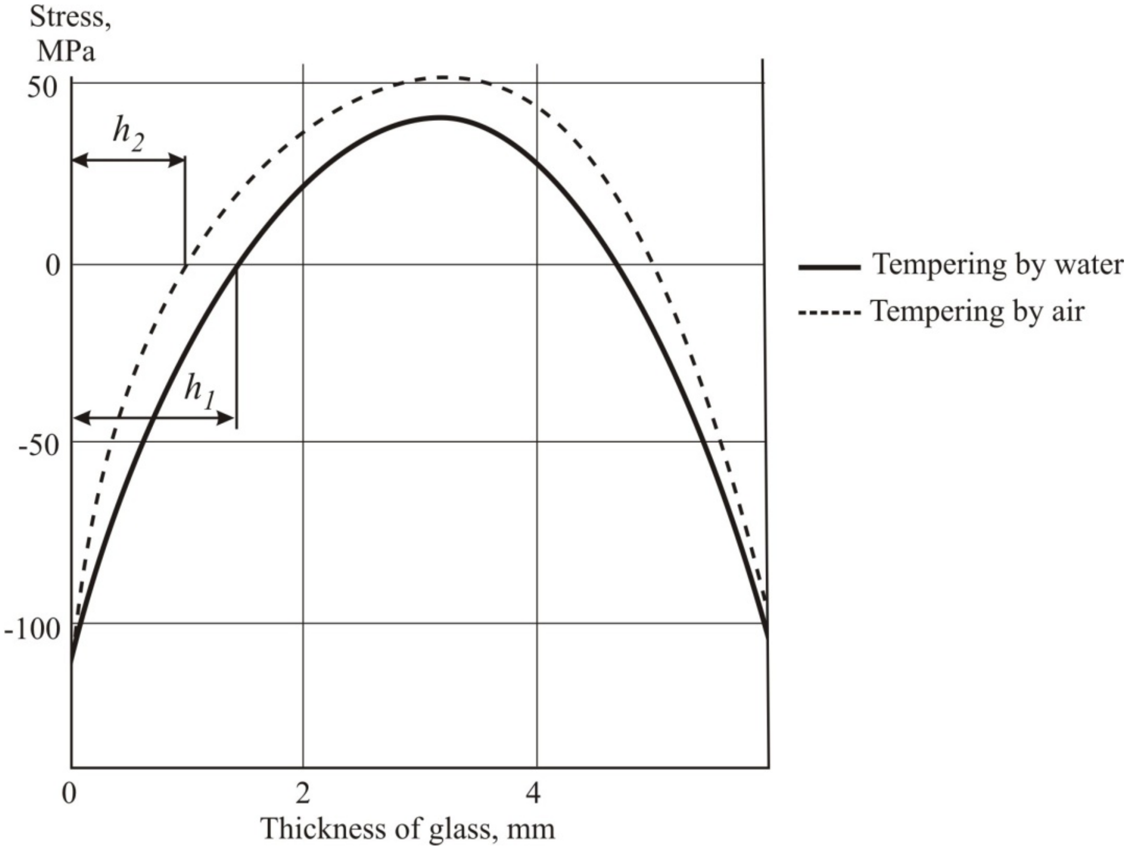
***Abstract* – A new energy-saving and efficient method of glass tempering by using water as a cooling agent is described. This glass is not inferior to the strength of traditional tempered glass. In addition, it does not fall to pieces during drilling and cutting and it is characterized by higher chemical resistance and microhardness.**

Keywords – float glass, tempering, acid resistance, microhardness, stresses, stress diagram, electricity consumption.

Research Results

In connection with the growth of pace of building and mechanical engineering development nowadays tempered glass has more and more applications. This glass features much greater strength compared to ordinary float glass. In addition, its important advantage is that after breaking it does not form large debris. It falls to small pieces with blunt edges, which can not cause significant injuries to people. This feature is important for window glazing of top floors of multistory buildings, as well as for side and rear windows of cars. For front windows of cars triplex with semi-tempered glass is applied. This glass has slightly lower strength compared to tempered one, but after breaking it preserves the integrity of the window and allows a driver to get to the repair service.



Fig, 1. Diagram of stress distribution in glass tempered by water and air (thickness of compressed layer h1 = 1,4 mm h2 = 1 mm).

Despite the significant advantages, tempered glass has also a number of drawbacks. The first disadvantage is the high cost and energy intensity of modern method of glass tempering. In order to temper glass, it must be heated to the temperature of 600-700 °C, and then is blown for 10-20 seconds by ventilators with the power of 600 kW. In order to get semi-tempered glass, which is put into front windows of cars, it is cooled by air heated to 80-400 °C. This makes the glass even more expensive.

After tempering stresses are formed in the volume of glass, the distribution of which is described by a diagram in the form of parabola. Its edges indicate the amount of compression stresses on the surface, and the placement of peak in the diagram depends on the maximum amount of tensile stresses in the middle layer of glass. The compressive stresses (fig. 1) on the surface are approximately 110 MPa, and the tensile stresses in that glass are 50 MPa. The permissible value of tensile strength of float glass which is taken at the calculations is 30 MPa. Thus, during cutting or drilling, tempered glass will fall to pieces as soon as the cutting tool reaches the zone of location of destructive tensile stresses.

Furthermore, as a result of traditional tempering the microhardness and chemical resistance of glass decreases.

Elimination of all above-mentioned drawbacks can be done by introducing into production our patented method of glass tempering by water cooling [1, 2]. The method consists in the fact that before heating the glass is fixed between two heat-resistant and heat conductive plates. After that, this complex is heated in a furnace to the tempering temperature, and its cooling is carried out by spraying the plates with ordinary water. The heat conductive plates make it possible to distribute evenly the cooling effect of water throughout the entire surface of heated glass. If heated glass surface is watered without such plates - the glass will break. The reason for this is uneven cooling, which occurs due to the formation of heat-insulated zones in places of water evaporation.

Glass tempered by the proposed method is not inferior to the strength of traditional tempered glass, but is much cheaper. Average electricity consumption of traditional tempering method is about 100 kWh, and in the proposed method it is only 10 kWh. In addition, the tensile stresses in the middle layer of such glass are approximately 30 MPa (Fig. 1), which means that it can be cut and drilled. The obtained results (fig. 1) make it possible to estimate the thickness of the compressed layer in tempered glass. As a result of water cooling, this thickness rises from 1 mm to 1.4 mm. This indicates that the introduction of the new glass tempering technology will also increase the operational reliability of glass (scratch resistance).

Another advantage of the proposed method is that it also allows to obtain obsemi-tempered glass by increasing the thickness of heat conductive plates.

Research indicates that the reason of reduction of microhardness and chemical resistance of draditional tempered glass is uneven cooling that occurs during the air blowing of hot glass. In this case, zones of overstresses that cause these deterioration of surface properties are formed. The usage of heat conductive plates at glass cooling with water allows to make it more uniform. As a result, the microhardness of tempered glass rises from 5300 MPa to 5400 MPa, while the mass loss after the acid resistance test decreases from 2.5 mg/dm2 to 2.2 mg/dm2.

Conclusion

Therefore, the proposed method of tempering glass not only allows to increase glass strength at the level with the traditional, but also has a number of advantages. This includes lower cost, greater energy efficiency, higher microhardness, chemical resistance and operational reliability.

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Formation of Nanostructured Copper Electrodes for the Conversion of Carbon (IV) Oxide

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Abstract* – *The basic conditions for the formation of nanostructured copper electrodes by depositing silver sols from solutions of complexes in an environment of an organic proton solvent dimethylformamide (DMF) are established. Their comparative catalytic activity for the conversion of carbon (IV) oxide has been investigated.

Keywords – galvanic replacement, nanostructured electrodes, electrolytic copper, silver, carbon (IV) oxide, conversion.

Introduction

The increasing level of carbon dioxide in the atmosphere is one of the main causes of global climate change. Among numerous strategies for its removal, storage, and reuse, electrochemical conversion of CO_2 to chemicals or high value-added fuels is considered the most effective approach [1, 2]. However, the conversion linear CO_2 molecular is a kinetically slow reaction due to its low electron affinity and other energy factors. Therefore, much effort has been devoted to developing a variety of metallic catalysts. In particular, one of the effective approaches for enhancing the catalytic action is to modify metal electrocatalysts in Ag, Au, Pd, and Pt nanostructures. By alloying of various metals, we might be able to adjust the binding strength of intermediates on the catalyst surface by means of the synergistic geometric and electronic effects between metallic components. A change in the binding strength of intermediate compounds causes a change in the reaction kinetics, as well as nature final products of CO_2 conversion.

One of the promising methods for modifying the surface of metal electrodes with nanoscale particles is a galvanic replacement [3, 4]. However, the spontaneity of this process makes it difficult to obtain nanoparticles with given characteristics — geometry, size distribution, and component content. Therefore, it is relevant to establish the basic parameters that affect these characteristics.

The aim of the work was to establish the conditions for the formation of nanostructured copper electrodes for carbon (IV) oxide conversion by depositing silver precipitates in an organic aprotic solvent (DMF), which is a continuation of systematic studies on the modification of metal and semiconductor surfaces by mono- and bimetallic by galvanic replacement [3, 4].

Research Results

It has been established that on the surface of electrolytic copper (from acidic sulfate and pyrophosphate electrolytes), nanostructured silver deposits are formed by galvanic replacement in dimethylformamide solutions. High-donor properties of dimethylformamide make the formation of surface complexes on the germs of renewable silver similar to the action of surfactants, which positively affects the nanostructure of the sediment. Unlike water, the polar molecules of DMF, due to higher electron donor properties, form a solvent $[Ag(DMF)_n]+$ soluble in Argentum, which cause cathode polarization, which also causes the formation of nanoscale spheroidal silver particles.

It is shown that the main parameters of the influence on the morphology of silver sediment and the geometry of its structural particles are the nature, and composition of the solution, temperature and duration of the process. Micro and nanostructured silver sediments are formed in solutions of complexes of reducing metals $[Ag(CN)_2]^-$, $[Ag(NH_3)_2]^+$, $[Ag(SC(NH_2)_2)_2]^+$ on copper surfaces. With increasing stability of the complex there is a tendency to decrease the size of metal particles on the substrate surface. In particular, in solutions $[Ag(CN)_2]$ nanoparticles of up to 100 nm is formed with a relatively small range of their sizes.

As the concentration of the complex in the solution decreases, there is also a tendency to decrease the size of the particles of reducing silver, which is caused by concentration polarization. Increasing the temperature and duration of galvanic substitution contributes to the growth of particles and the formation of film sediment on the surface of electrolytic copper.

The comparative catalytic activity of the conversion of carbon (IV) oxide in 0.1 M $KHCO_3$ aqueous solutions saturated with CO_2 was studied on the copper cathodes obtained by modified nanostructured silver galvanic replacement. The analysis of cyclic voltammetric curves has shown that high catalysis activity is characterized by cathodes with a developed surface, obtained by electrochemical deposition of metal from acidic sulfate electrolytes. Modification of copper electrodes by nanostructured silver from cyanide complexes contributes to the deep conversion of carbon (IV) oxide.

Conclusion

In solutions of Argentum complexes, submicronous and nanosized silver particles with uniform distribution on the substrate surface are formed by galvanic replacement on the surface of electrolytic copper. During the recovery of silver from solutions of stable cyanide complexes in a DMF medium, discrete metal particles up to 100 nm are formed, which facilitates the modification of the surface of copper by nanostructured sediments. The increased catalytic activity of copper electrodes modified by silver from cyanide complexes is due to synergistic and nanosized effect.

Acknowledgments

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Depth of Application of a Microgranule for Precision Sowing on the Controlled Release of Nutrients, and the Growth of Maize Plants in the Initial Stage of Development

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***Abstract* – The manuscript presents the results of vase experiments on the determination of the depth impact of soil microgranulate application for precision sowing on the growth of maize plants in the initial stage of development. Multi-component granule used in the experiment characterized by the controlled release of ingredients was made on the basis of an alternative source of a phosphate in accordance with the patent application No. P.429318.**

Keywords – alternative raw material, phosphorus, precision fertilization, soil-applied microgranula, maize.

Introduction

The innovative simplified technology of maize cultivation consists of the utilization of a cultivating and seeding aggregate, thanks to which seed sowing is performed at the same time as a deep precise application of fertilizer to cultivated soil [Ochal i in., 2015].

Aim and Scope

The purpose of the pot experiments was to determine the effect of the depth of application for precision sowing of microgranules developed on the basis of an alternative source of phosphorus originating from thermally processed bone waste (patent application No. P. 429318) for the growth and development of corn at the initial stage of development.

Methodology

Table 1

Composition of microgranules for precision sowing

Content of makro- and mikroelements								
P_2O_5	K_2O	CaO	MgO	Na_2O	Mn	Fe	Cu	Zn
314,0 $g \cdot kg^{-1}$	42,3 $g \cdot kg^{-1}$	663,1 $g \cdot kg^{-1}$	240,3 $g \cdot kg^{-1}$	5,4 $g \cdot kg^{-1}$	6,5 $mg \cdot kg^{-1}$	1 $mg \cdot kg^{-1}$	3,2 $mg \cdot kg^{-1}$	0,8 $mg \cdot kg^{-1}$

The pot experiments were carried out under strict conditions in the vegetation greenhouse. Standardized soil, a mixture of sand and acidified peat with a pH of 5.5-6.5 in the ratio of 7: 1, was used in the experiment and certified maize seeds of the variety Farm Gigant (MTZ = 264g) were utilized. The developed microgranule (table 1) for precision sowing at a dose of 30 kg ha-1 was applied at the depth of: 2, 4, 6, 8 and 10 cm in relation to the kernel in the Fix system. The experiment was carried out at a constant soil moisture of 50% PPW.

Results and Discussion

Based on the pot experiments on the depth of application of microgranules for precision sowing with controlled release of components, it was found that the highest growth and development of maize plants occurred in a variant in which the fertilizer was applied at a depth of 2 cm to the kernel. The location of microgranules at a depth of 2 cm from the kernel resulted in obtaining the highest parameters of biometric traits of maize plants in the 6th week of sowing (Fig. 1).

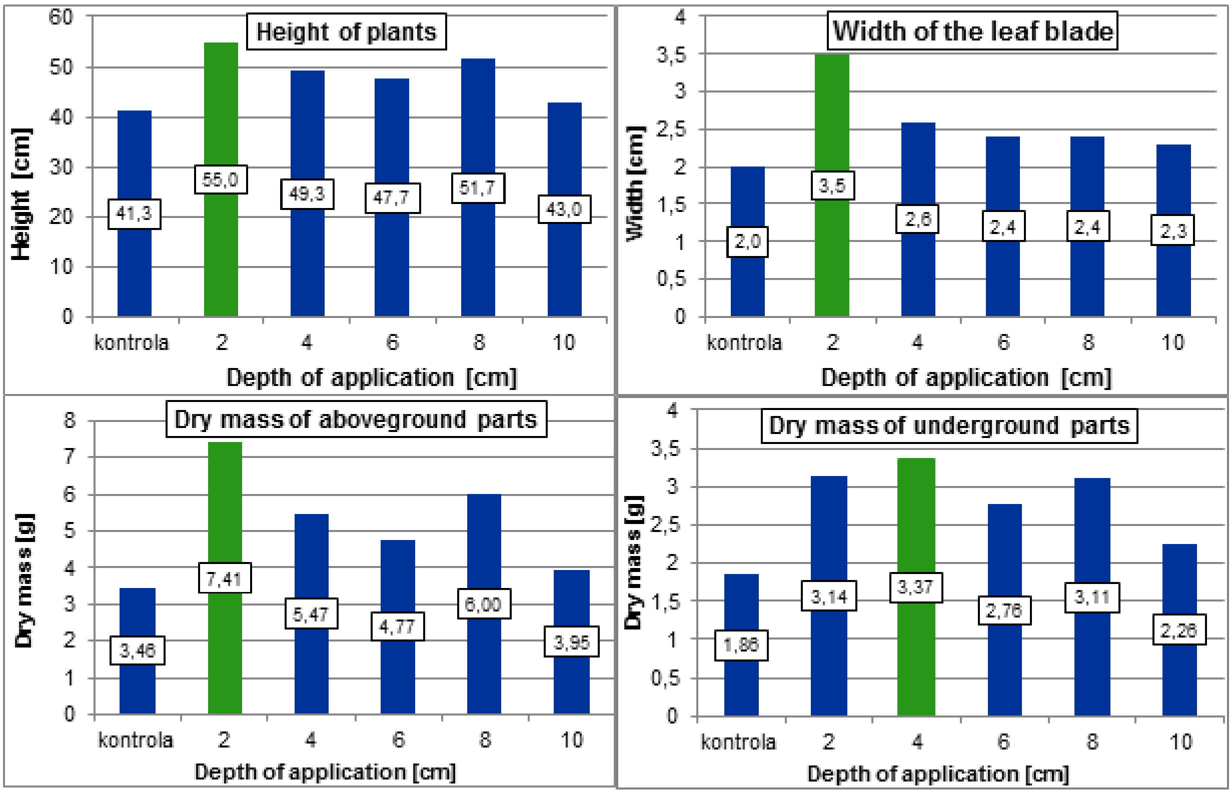

Fig.1. Biometric features of maize plants depending on the depth of application of the fertilizer

Conclusion

The application of a multi-component fertilizer with a controlled release of ingredients at a depth of 2 cm in relation to the kernel, developed on the basis of an alternative source of phosphate, results in the best growth and development of maize plants in the first 6 weeks of sowing.

Acknowledgments

The research was carried out as part of the project "Development of innovative fertilizers on the basis of an alternative source of raw material" No. BIOSTRATEG1 / 270963 // 6 / NCBR / 2015 co-financed from public funds at the disposal of the National Center for Research and Development under the "Environment, Agriculture and Forestry" Program - BIOSTRATEG.

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Use of Ultrasound in Rape Oil Extraction Process

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Abstract* – *An extraction method for the production of vegetable oils is essential in the food industry. Getting oil in this way is the most economical, provides maximum degreasing of oilseeds, and allows you to achieve high quality of the product. The main advantage of the extraction method of obtaining vegetable oils in comparison with the press is the significant increase in the yield of oil, even in the processing of low-oil seeds.

Keywords – asphalt concrete, modifier, epoxide, bitumen, strength, water resistance, ultrasound.

Introduction

All extraction processes are limited by diffusion at the interface of the phases through a diffusion layer with gradient concentration of the extraction of matter. Traditional extraction methods are long-lasting. Ultrasound can significantly accelerate the extraction process, increase output, reduce the cost of extraction of matter and improve the quality of the product.

The influence of ultrasonic oscillations with 22 kHz frequency, low resonance cavitation (17-100 Hz) and vibration turbulent devices on the output, composition of extraction products was investigated and analyzed. It has been shown that in all cases the yield of the extract increases, but the quantitative characteristics of the product obtained are different.

The process of epoxidation of obtained extracts and their application in the process of modification of road bitumen was investigated. Taking into acount the considerable time of the modification process, and some differences in the results obtained in studies using oils obtained by different extraction methods, a decision was made on the need to intensify the processes of modification of road bitumen by use of ultrasound [1].

Different methods of extraction, their advantages and disadvantages were considered. Some conclusions are made about the use of ultrasound in the extraction process for the production of oils, and in the process of modifying of road bitumen with epoxy compounds.

Conclusion

The use of cavitation in the process of modifying of road bitumen for reducing of the modification time, comparative analysis of the properties of bitumen, modified using cavitation and without it, as well as the study of the effect of these changes on the properties of asphalt concrete were made. The industrial use of the obtained, high-quality and cheap vegetable-based modifier will promote the expansion of the use of BMP and, consequently, increase the durability of road coverings.

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Research of Properties of Raw Cotton –as the Object of Drying

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Abstract* – This article presents the results of the study of the properties of raw cotton with a multi-purpose scanning electron microscope, which combines the possibilities of working in both standard and low-vacuum modes. On cross sections of the fibers, three zones are noticeable, differing in microstructure and relation to the action of the reagents. The hygroscopicity, tensile strength, heat resistance, chemical properties, resistance to biological destruction, the structure of cotton are determined. On cross sections of the fibers, three zones are noticeable, differing in microstructure and relation to the action of the reagents. Zones A correspond to places with a higher density of the fibrillar structure and, therefore, the lowest availability for reagents. Zone B has a well-oriented structure of concentric layers, but more changes under the influence of reagents. Zone C is characterized by an unorganized and looser structure, so the fiber here is easier to react with. Inside the fiber passes a channel that is filled with air in a mature fiber. For cotton fiber, 11 maturity groups have been established, characterized by a coefficient of maturity - from 0 to 5 points.

Keywords – filtration drying, hydrodynamics, fibrous materials,, moisture, thermal agent, heat-mass transfer, diffusion.

Introduction

During the drying of raw cotton, its temperature rises slightly, which will lead to a deterioration of the technological properties of the fiber. If the temperature rises during drying of raw cotton, a lot of moisture is lost, which leads to the rupture of each fiber. Each variety of raw cotton has its own specific to physical factors. The fiber has a mechanically bound moisture that easily evaporates from the surface area as from the free surface of the liquid. The movement of moisture and the mechanism of evaporation of water from the seeds depends on the level of interacting factors. The choice of raw material drying mode strongly depends on the following parameters: color, fiber length, type of mechanical damage, etc. In case of improper drying, fiber breakage is observed, its length is reduced, as a result, the quality of the fiber in The processing of raw cotton for more efficient and high-quality fiber, their humidity should be within 8-9% [1,2].

Result of Research and Discussion

Result of Research and Discussion

To determine the properties of raw cotton, a multi-purpose scanning electron microscope (useful magnification of 300 000) was used, which combines the capabilities of both standard and low-vacuum modes. Allows you to examine samples without spraying with a conductive layer. Additionally equipped with energy dispersive microanalysis system INCA Energy 350 and a prefix for the study of texture and structure of polycrystalline samples HKL Basic

The breaking strength of cotton fiber, depending on the degree of maturity and variety of its ranges from 0.5 to 10 SN/fiber. The average strength of Mature fiber is 4-6 SN/fiber. Fibers having a strength of up to 2.5 SN/fiber are non-discharge. The relative breaking load varies from 24 to 36 SN/Tex depending on the breeding varieties of cotton and the degree of maturity of the fiber[1, 2].

The elongation of the fiber at break is on average 7-8%, which is explained by the spiral arrangement of cellulose layers in the fiber wall. Cotton fibers have a small elastic and large plastic elongation. Because of the low elasticity fiber textile products of cotton crumple easily, they formed derepresses folds and samini.

Under normal conditions, the moisture content of cotton fiber is 7-9%. To the action of water, both cold and hot, cotton fiber is resistant. When heated in hot water (up to 150 °C) under pressure, the properties of cotton also do not deteriorate. In the water environment, cotton fiber swells, increases in diameter by 15-30% depending on the temperature and duration of treatment. The swelling of the fiber is accompanied by an increase in its tensile strength by 15-17%, which is explained by an increase in the degree of orientation of cellulose macromolecules in the direction of the tensile load.

The thermal resistance of cotton fiber is quite high. Moistened fiber is not destroyed at a temperature even above 250 °C. As long as the moisture from the fiber is removed by evaporation, its temperature does not exceed 100°C. However, after moisture loss, the fiber is quickly destroyed to form a variety of liquid and gaseous products. At a temperature of 400-450 °C, the fiber is charred. The fiber can withstand short-term heating to a temperature of 120-150 °C.

Under the action of mineral acids cotton fiber is destroyed by hydrolysis of cellulose. The alkali resistance of cotton fibers is very high: even when boiling in alkaline solutions without oxygen, the fibers are almost unchanged. But when boiling in solutions of caustic alkalis with air access, the mechanical strength of the fiber decreases due to the oxidation of cellulose.

OPTIMIZATION OF BIOCHEMICAL PROCESSES AND BIOENGINEERING

The effect of short-term exposure of esters of thiosulfoacid on the phospholipids spectrum of hepatocytes

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Abstract* – *Administration of esters of thiosulfoacid on the phospholipid profile of liver in rats were studied. It has been shown the significant effect of allyl and methyl esters of thiosulfoacids on the ratio of phospholipid fractions in hepatocytes that is accompanied by a change in structural and functional characteristics of membranes.

Keywords – esters of thiosulfoacids, phospholipids spectrum, hepatocytes, rats

Introduction

A series of esters of thiosulfoacid have been synthesized in the Department of Technology of Biologically Active Substances, Pharmacy and Biotechnology. Esters of thiosulfoacids are widely used in pharmacology, medicine, and agriculture. These compounds are characterized by a wide range of biological activity, which makes them promising substances for the development of effective therapeutic agents [1]. As fat-soluble compounds, they easily penetrate membranes inside the cell, realizing their biological effects. Therefore, the purpose of our work was to study the effect of short-term exposure of S-esters of thiosulfoacids on the phospholipid spectrum of the liver in the rat.

Results and discussion

The effect of allyl-4-aminobenzenethiosulfanilate, ethyl-4-aminobenzenethiosulfanilate, and methyl-4-aminobenzenethiosulfanilate were studied in experiment. Studies were carried out on Wistar rat male with body weight 190-210 g, which were injected intraperitoneally by oil solutions of esters at the dose of 300 mg/kg of body weight once a day for 3 days. Animals of the control group were given an appropriate dose of sterile oil. The total content of phospholipids and their spectrum in liver tissues were determined.

The short-term exposure of synthesized esters of thiosulfoacid at a dose of 300 mg / kg of body weight did not significantly affect the total content of phospholipids in the liver of rats, but led to changes in the ratio of their fractions. Allyl and methyl esters of thiosulfoacid have the greatest impact on the phospholipid profile of hepatocytes. After administration of allyl esters of thiosulfoacid, the asymmetry ratio of hepatocyte membranes decreased significantly compared to control animals, indicating an increase in the saturation of lipid bilayer and an increase in the viscosity of the membrane. In contrast to allylthiosulfanilate, methyl ester of thiosulfoacid positively influenced on the structural and functional characteristics of cell membranes, increasing their fluidity.

Conclusion

Redistribution of different fractions of phospholipids in liver tissue in response to the short-term exposure of synthesized esters of thiosulfoacid is the result of adaptive-compensatory reactions of the organism of rats and is associated with their participation in various physiological processes.

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Changes in plant material when drying according to IR spectroscopy

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Abstract – Infrared spectroscopy of parenchymal tissues of apples subjected to heat drying has shown an increase in the structural hardness of carbohydrates in the removal of water hydrated by them and a gradual violation of the structure of proteins under the influence of heat and dehydration.

Keywords – drying, infrared spectroscopy, parenchymal tissues, carbohydrates, proteins.

Introduction

Classical representations about mechanisms of dehydration of colloidal capillary-porous bodies, that sort are plant tissues, are based on the assumption that water is hold up owing to by osmosis, capillary condensation and adsorption. In doing so, the following characteristics of the material, such as porosity and the differential function of the distribution of pores from the radii, are taken into account. Very rarely, using the introduction of chemical potential, the influence of the chemical composition of the material is taken into account. But vegetable fabrics differ both in the wealth of chemical composition, and in the ability to change it under the influence of technological factors. The features of structural and chemical changes in the material can be register both in its physic-chemical and spectral characteristics. This kind of work for complex biological objects only began [1, 2]. The purpose of our work is to study with the help of infrared spectroscopy of structural and chemical changes of plant tissues under the influence of technological factors of the drying process (heat and dehydration).

Research results

The study was carried out by infrared spectroscopy of the affected full internal reflection. For the experiments, thin (~ 1.5 mm) sections of the parenchymal tissues of the "Glory to the Winner" apples were used, which were dried in an air flow of 3 m/s at a temperature of 60 °C to obtain specimens of varying degrees of moisture. The spectra (Fig. 1) were made on an Fourier Spectrometer VERNEX 70 (Bruker), equipped with the software package OPUS ™, with standard calibration capabilities, in the 4000 … 400 cm^{-1} frequency range in transmission format.

Based on the spectra obtained, it is possible to identify the variations of the main groups of the main components of the apple – water, sugars, fiber, hemicellulose, proteins and and. Spectra of apples of different humidity are similar in appearance. The effect of the degree of dehydration on the structure and composition of the tissues appears in detail. In the broad high-frequency absorption band with a maximum of 3310 cm^{-1}, there may be bands of valence fluctuations NH_n- and OH-groups of all the major biocomponents, but a sharp decrease in the maximum of this band during dehydration indicates the predominance of valence fluctuations in OH groups of water. Intensity decrease of the high-frequency shoulder of the band in the region of 3000 ... 2820 cm^{-1}, with reduction of the moisture content in the samples, the bands of valence vibrations of the CH_n-groups of all components are clearly manifest. This may indicate an increase in the structural stiffness of the carbohydrate blocks during drying. The bands in the region 1750 ... 1540 cm^{-1} belong to the carbonyl C=O-groups and indicate the presence of free carboxylic acids and protein components in the experimental samples. The gradual decrease of the intensity of these bands may indicate degradation and/or violation of the structure of proteins under the influence of temperature (t ≥ 60 °C) and dehydration. There is also a gradual evaporation of carboxylic acids. In the region of 1400 ... 990 cm^{-1}, oscillations of the C–O-bonds of mono-, oligo- and polysaccharides are usually manifested. Strengthening their intensity during dehydration indicates the transformation and strengthening of the structure of the carbohydrate components of the apple in the removal of hydrated water. Proportional from of the degree dewatering of the decline of the intensity of the complex band in the range 900... 400 cm^{-1} allows it to be identified as deformation vibrations of different on sized associate molecule water.

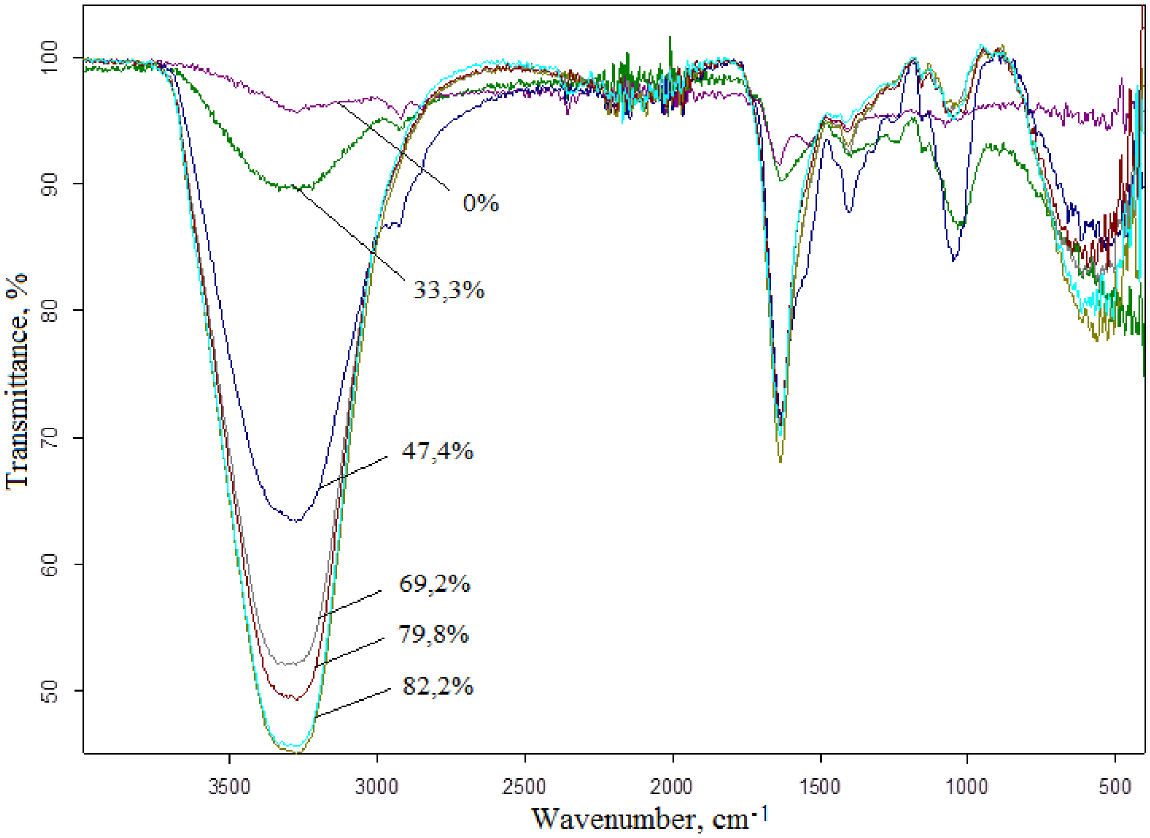

Fig.1. Infrared spectra of parenchymal tissues of apples of different degrees of humidity.

Conclusion

The conducted study allowed observing different sensitivity of carbohydrate and protein structures of the apple to the effect of heat and dehydration. The growth of structural rigidity of mono-, oligo- and polysaccharides in the removal of hydrated by them water. Gradual violation of the structure of proteins under the influence of temperature 60 °C and dehydration.

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Hydrogel films of membrane type for biomedical application on the basis of polyvinylpyrrolidone copolymers

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Abstract* – The kinetic of copolymerization of 2-hydroxyethyl methacrylate (HEMA) with polyvinylpyrrolidone (PVP) in aqueous-organic media was investigated. The optimal initiating systems and the temperature regimes of the polymerization for fabrication of hydrogel film membranes based on HEMA/PVP copolymers were developed. The influence of the structure of the hydrogel film membranes synthesized with rare cross-linked copolymers on their the basic operational properties was established.

Keywords – polyvinylpyrrolidone, cross-linked copolymer, hydrogel, film membrane.

Introduction

Hydrogel materials based on 2-hydroxyethyl methacrylate with polyvinylpyrrolidone rarely cross-linked copolymers are used effectively for the manufacturing of contact lenses, polymer carriers of drugs, medical bandages, removable dentures in dentistry, as implants in plastic surgery etc [1] – [3]. Such materials are usually used in the form of films, which, at the same time, serve as membrane functions. The most common method for obtaining film membrane hydrogels is the polymerization of compositions in an aqueous medium or a water-soluble organic solvent, which after synthesis is replaced with water or aqueous solution [3], [4] . Operational and technological properties of hydrogel copolymers, including permeability and sorption ability, are largely determined by their composition and structural parameters of the network. Therefore, it is important to search for effective methods of directed formation of the structure of copolymers, which will allow to predict the operational properties of hydrogels on their basis. The aim of the work was to develop the foundations of technology and modes of formation of hydrogel membranes based on compositions of HEMA with PVP with an adjustable structure and composition of copolymers.

Experimental Set-up and Procedure

For researches used: 2-hydroxyethyl methacrylate HEMA (Bisomer® trademark), purified by distillation in a vacuum (the boiling points is 78 °C, under a residual pressure is 130 N/m2); polyvinylpyrrolidone PVP10 with a molecular weight of 10·103 (SIAL Sigma-Aldrich® trademark) pharmaceutical purification. Experimental samples of hydrogel film membranes were obtained by copolymerization HEMA with PVP in a solvent medium between two glass plates. The distance between the plates determined the required thickness of the film. The kinetics of polymerization was studied by the chemical method by reducing the amount of unreacted monomer. The fraction of PVP, which entered into the reaction of grafted polymerization, was determined by photocolorimetric method. The sorption properties of hydrogels with respect to water were determined by the weight method, the mechanical properties – by the method of film breakage in the aqueous medium, the permeability of the membranes for water and dissolved substances in it – by the method of osmosis.

Results and discussions

Studies in the kinetics of polymerization have found that the addition of PVP to the composition significantly increases the rate of polymerization. The polymerization is affected by the physical interaction between the components of the reaction medium through the so-called “matrix effect” with the formation of a charge-transfer complex. To investigate the initiator's influence on the polymerization of HEMA in the presence of PVP and the choice of the optimal initiator and its amount, the reaction was initiated by benzoyl peroxide (BPO), potassium persulfate (KPS) and azo-bis-isobutyric acid dinitrile (AAD). The rate of polymerization increases in the series AAD – BPO – KPS. For peroxide initiators, the rate of polymerization reaction is greater, which is obviously due to the promotional effect of PVP on the decomposition of peroxides.

Investigations of the influence of the nature of the solvent on the polymerization process revealed that the highest polymerization rate of HEMA in the presence of PVP is observed in an aqueous medium. In water, the compositions polymerize at high speed, even with a large dilution with a solvent at low temperatures (55…65 °C). This enables the synthesis of hydrogel membranes on their basis in mild conditions and to avoid unwanted exothermic effects. On the basis of kinetic studies, the two-stage mode of formation of film hydrogels is substantiated: 1 stage – 55 °C (2,5 hours), 2 stages – 70 °C (3 hours).

Hydrogels on the basis of copolymers PVP with HEMA are cross-linked and consist of macromolecules PVP, to which grafted chains polyHEMA. The course of graft polymerization is confirmed by IR spectroscopy, differential-thermal and thermogravimetric analyzes. For all compositions with different contents of PVP there is an increase in efficiency and an extreme change in the degree of grafting over time.

The porosity of film hydrogels, which determines their permeability, can be controlled by polymerization in the presence of different amounts of solvents (Table 1). In this case, the porosity depends on the amount of solvent in the initial composition for the constant ratio monomer: PVP.

Table 1

Influence of composition content, nature and amount of solvent on the structure and properties of hydrogel membranes (polymerization regime: 55 °C – 2,5 h, 70 °C – 3 h; [KPS] = 0,25 % mass)

Content of the components, mass p.				M_n, kg/mole	σ, MPa	W, %	Permeability coefficient*	
HEMA	PVP	H_2O	DMSO				$k_{H_2O}\cdot 10^3$, $m^3/(m^2\cdot h)$	k_{NaCl}, mole/$(m^2\cdot h)$
10	–	10	–	12	0,53	42	0,51	80
9	1	10	–	20	0,46	45	2,90	141
8	2	10	–	24	0,40	48	5,23	181
8	2	9,9	0,1	25	0,40	52	5,30	–
8	2	9	1	34	0,41	47	5,65	212
8	2	8	2	46	0,41	47	6,24	240
8	2	–	10	63	0,42	–	7,10	272
8	2	20	–	28	0,38	55	7,42	234
7	3	10	–	38	0,31	53	7,14	232
5	5	10	–	51	0,22	61	10,2	274

DMSO – dimethyl sulfoxide; M_n – internodal molecular mass; σ – tensile strength;
W – water content; * – thickness of the hydrogel film is 200 μm

The grid density, which is determined by the molecular weight of the internodal fragment Mn, is a measure of permeability in the case of a defect-free structure. However, the content of the solvent in the initial composition, which exceeds its maximum content during the equilibrium absorption of the polymer matrix, has a natural phase separation, which manifests itself in the turbidity of the film.

The researches have established that by selecting the nature of the solvent (protonodonor or aprotic, or a mixture thereof), it is possible to adjust the density of the mesh of the hydrogel membrane [4]. Changing the density of the net affects the permeability of the membrane for low molecular weight substances (Table 1). Strength during stretching of membranes at the same time practically does not change.

The greatest influence on the structural parameters of the grid and permeability was observed when small amounts of dimethyl sulfoxide were added to the water. These parameters were subsequently virtually unchanged for more than 30% by weight of dimethyl sulfoxide of total solvent. At the same time, hydrogel membranes based on HEMA and PVP copolymers are characterized not only by increased sorption properties (compared with homopolymers HEMA), which were estimated by water content but also several times more permeability for water and aqueous solution of a model substance (sodium chloride) (Table 1).

Conclusions

According to the proposed method for forming the structure of the hydrogel, the porosity of the membrane is directed to change the density of the polymer matrix grid, which results in a controlled change in permeability. The strength of the membranes based on HEMA–PVP copolymers at the same time vary slightly. The performed researches are the basis of the developed method of regulation of the structure and properties of hydrogels [4] and membranes on their basis.

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Research of the rheological properties of the gel based on sodium alginate for the local treatment of burns

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***Abstract* – gels are the most common dosage form for the local treatment of burns, which are safe and easy to use. Important gel parameters are rheological characteristics, such as shear stress, dynamic viscosity, mechanical stability that can predict the behavior of the environment in technological processes, and they are important for the creation of new and improved existing drugs.**

Keywords – dynamic viscosity, mechanical stability, thixotropic properties, gels, sodium alginate.

Introduction

Burns are one of the most common types of injuries. According to the World Health Organization, 180 000 deaths from burn injuries are recorded annually in the world. Burns occupy third place (up to 10%) among all types of injuries among the civilian population and occupy about 5% of injuries on the battlefield. In 2017 from burn injuries suffered in Ukraine 7605 children [1].

The study of the range of medicinal drugs registered in the pharmaceutical market of Ukraine, according to the State Register of Medicines and the Anatomic-Therapeutic-Chemical Classification, proves the prospect and feasibility of the creation of new drugs in soft forms.

In recent years, gels are the most common dosage form for the local treatment of superficial burns that are becoming increasingly popular among soft dosage forms [1]. Gels are safe for the skin and easy to use, evenly distributed on the burns surface, forming a protective film, exhibit cooling effect upon application to the skin by evaporation of water, provide uniform release of the active pharmaceutical ingredient, and are economically affordable.

Important gel parameters are rheological characteristics, which can predict the behavior of the environment in the technological processes, and they are important for the creation of new and improved existing drugs. The rheogram estimates the type of flow, as well as the presence of thixotropic properties. It is a known fact that a thixotropic phenomenon is the slow change in the viscosity or any rheological properties caused by deformation of the material or its restoration after removing external influences. Thixotropic properties also complemented by the presence of electrolytes, pH and temperature [2].

Study of rheological properties important and necessary for the creation of liquid and soft medical forms [3].

The purpose of the work was to study the rheological (thixotropic) properties of the developed gel.

Experimental Set-up and Procedure

Taking into account the above and based on the results of the performed researches, the composition and technology of the combined drug in the form of a gel (base - sodium alginate 2%) containing a water extraction from xenoderms powder and lidocaine hydrochloride was substantiated, the technological scheme of gel production was developed.

The rheological properties of the gel were investigated using a rotatable viscometer Rheomat-30 firm Contraves AG (Switzerland) using rotary type of adapter with coaxial cylinders (measuring system cone-cylinder CM 409.475, volume of the test sample was 0,9±0,1 см^3).

The viscometer is equipped with a liquid circulation thermostat UH-8 of the firm "MLW" (Germany). The studies were carried out in the range of speeds from 0 to 452 s-1.

The weight gel was transferred to the measuring cylinder, warmed for 20 minutes to the set temperature (20 oC, 35 oC, 50 oC), after which the device was switched on and the cone began to rotate from the small deformation rates while fixing the viscometer's fixes. Gradually increased the speed (from 1 to 30) of rotation, while fixing the displays of the device. At the maximum speed (degree 30) within 15 minutes, the structural framework of the gel sample was destroyed. The device switched off, leaving the gel alone at rest for 15 minutes, after which made measurements, reducing the speed (of 30 to 1).

We obtained the dependence curve of the shear stress (τ, Pa) on the velocity gradient (Dr, s-^{1}).

Shear stress (τ, Pa) was calculated by using the formula:

$$\tau = \tau_r \cdot \alpha,$$

where: τr – device constant, Pa; α – display of the device.

The calculation of dynamic viscosity (η, mPa·s) performed according to the formula using the data of the shear stress:

$$\eta = \frac{\tau}{D_r},$$

where: τ – shear stress, Pa; Dr – velocity gradient, s-1.

The values of mechanical stability (MS), calculated by the formula:

$$\text{MC} = \tau_1 / \tau_2\,,$$

where: τ_1 – the strength of the structure to fracture; τ_2 – the strength of the structure after its destruction.

Results and discussions

Important indications of the soft dosage forms are their consistency and the ability to smear, which is related to the shear stress, as well as the stability of the gel when changing the temperature regimes of storage. The gel base should be easily applied on the damaged skin surface, have sufficient fluidity, facilitate release of the active ingredient from the dosage form. The dependence of the structure-mechanical properties of the gel on the shear rate was studied at temperatures of 20 °C, 35 °C and 50 °C in order to investigate changes in rheological parameters, as the temperature decreases the structure-mechanical and consumer characteristic of the gel (Fig. 1).

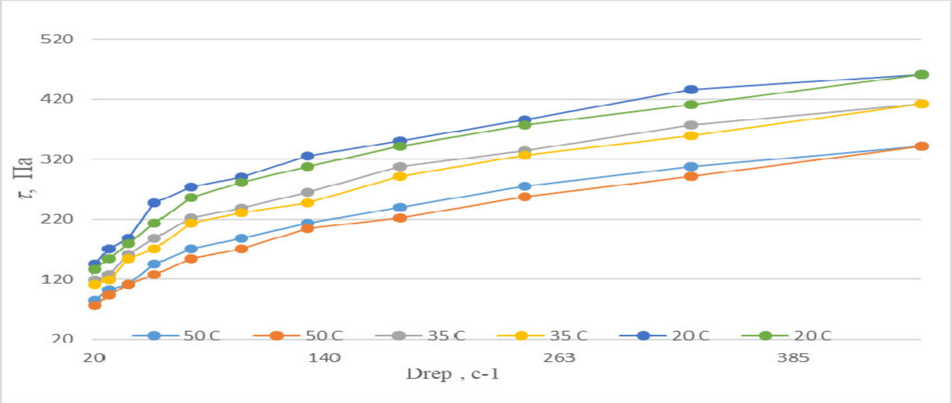

Fig.1. Rheogram of gel based on sodium alginate with lidocaine hydrochloride and water extract from xenoderms powder at a temperature of 20, 35, 50 ° C.

The rheogram of the experiment indicate that the gel under investigation is a non-Newtonian fluid and has a plastic type of fluidity. Figure 1 shows that gels based on sodium alginate characterized by the presence of the upper and lower curves of the flow that do not coincide with each other and form a "hysteresis loop" whose area indicates the presence of thixotropic properties despite the change in temperature regimes. At the same time, the area of the hysteresis loops is practically the same, but there is a regularity of reducing the bias voltage from the rate of displacement with increasing temperature of the experiment. With an increase in temperature up to 50 °C, a slight decrease in the viscosity of the gel is observed, which can be explained by heating the polymer molecule and changing the mechanical stability of the gel.

On Figure 2 shown the parameters of structural viscosity, which is make it possible to determine its dependence on the gradient of the shear rate at temperatures 20 °C, 35 °C and 50 °C.

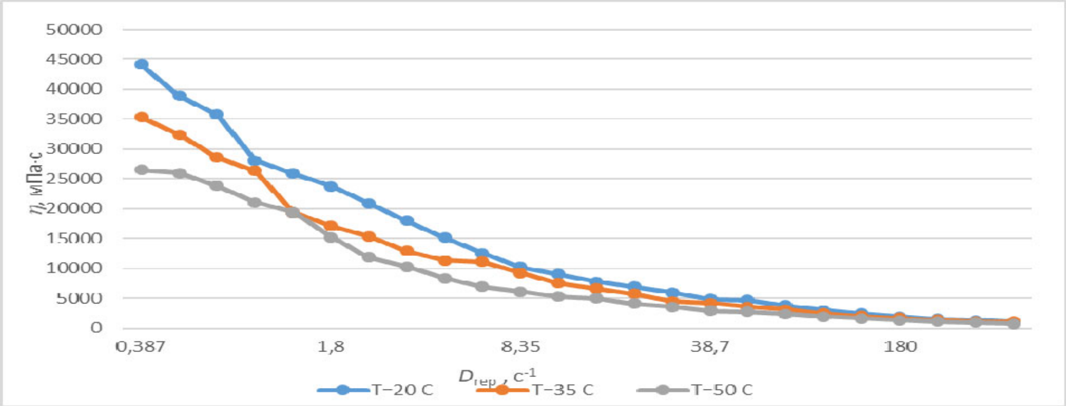

Fig.2. The dependence of the structural viscosity of the gel on the basis of sodium alginate (2%) on the shear rate at the temperature of 20 oC., 35 oC., 50 oC.

As can be seen from the data shown in Figure 2, there is a decrease in structural viscosity during the growth of the shear rate and temperature, which is logical for structured disperse systems based on sodium alginate, which in turn provides the necessary parameters of the process of gels.

Also, we have calculated the mechanical stability gels, which characterizes the degree of destruction of the polymer structure. The optimal value of mechanical stability is 1, at a temperature of 20 oC – MS = 1,06, at 35 oC – MS = 1,07, and at 50 – MS = 1,22, indicating no interaction between the active pharmaceutical ingredients and the base.

Conclusion

Was investigated the rheological properties of gel based on sodium alginate (2%) which is belongs to non-Newtonian types of solutions with plastic properties and exhibits thixotropic properties. The dependence of rheological properties, namely the viscosity of the investigated gel on the change in temperature regimes, has been confirmed. Calculated values of mechanical stability of gels, which allow predicting the stability of the drug.

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Nigella Damascena As An Object Of Biotechnological Research

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Abstract. One of the biotechnology directions is in vitro culture, actively used in the area of medicine and pharmacy. As a result of the research, the peculiarities of Nigella damascena introduction into the culture in vitro have been studied. Also, the optimal conditions for cultivation were selected, and the callus-like biomass of the Nigella damascena was obtained.

Keywords: Nigella damascena, in vitro, medicinal plant raw material, callus-like biomass.

Introduction

Modern biotechnology is a combination of technologies, involving the use of biological processes of living cells in order to obtain valuable biologically active substances. Therefore, we have paid our attention to Nigella damascena, which has a unique chemical composition and shows high pharmacological activity.

Studies in the 1990s of the 20th century have shown that plant oil greatly enhances human immunity and also has a strong antibacterial effect. The antibacterial property of Nigella damascena oil has shown high activity even against such bacteria as V. cholera and E. coli.

In addition, the seed contains an extremely important component - crystalline nigelone, as well as: 15 amino acids, 8 of which are essential; essential oils; alkaloids; saponin; proteins; cellulose; mineral salts (Ca, K, Fe, Mg, Se, Zn); vitamins A, B1, B2, C; about 45% of fatty oil, which contains 84% unsaturated fatty acids (of which 50-60% of linoleic acid and 20% of oleic acid) [2,3].

The aim of the research

Getting Nigella damascena callus-like biomass using the biotechnological method of tissues and cells culture in vitro.

Materials and methods of the research

The subject of the research was chosen the seeds of Nigella damascena.

For accelerated getting plants from seeds, the stratification with subsequent sterilization of seeds had been carried out. Stratification was carried out by soaking seeds in water for 24 hours. The sterilization was carried out with 70% ethanol for 10 minutes and 30% hydrogen peroxide for 10 minutes, followed by 3-time flushing of the seeds with sterile distilled water.

For cultivation of the plant seedling, we used the non-hormonal agar nutritional Murashige and Skoog medium and the hormone agar nutritional Murashige and Skoog medium to produce callus-like biomass [1,4].

Results of the research

The seeds, prepared with stratification and sterilization, were introduced into a sterile agar nutritional Murashige and Skoog medium.

The Petri dishes with seeds were placed into the thermostat at 23°C.

When using such a sterilization scheme: 70% ethanol - 10 minutes → 30% hydrogen peroxide - 10 minutes → 3-time washings with sterile distilled water → we received 99% sterile explants.

During 20 days, there were formed the plants of 5.0-7.0 cm, which we used as explants for further cultivation on agar nutrient Murashige and Skoog medium with growth regulators: 2.0 and 3.0 mg/L of IAA, 0.1; 0.5; 1.0 mg/L of NAA and 0.5 mg/L of kinetin.

The best results were obtained with a modified medium such as 3.0 mg/L of IAA, 1.0 mg/L of NAA and 0.5 mg/L of kinetin.

Cultivations were carried out: with photoperiod 16/8 h (light/ darkness), illumination 3000 lux, t 26°C (± 2-3°C), relative humidity 60-70%. After 60 days, the callus-like biomass of Nigella damascena was obtained.

Conclusions

The cultivation of Nigella damascena by tissue and cell culture in vitro had been carried out.

The optimal conditions for cultivation have been selected and it has been determined that explants form a callus on the Murashige and Skoog medium with the addition of growth regulators, namely: kinetin; benzylaminopurine; indoleacetic acid; 2,4-dichlorophenoxyacetic acid and 1-Naphthaleneacetic acid with a certain concentration and ratio.

In the future, the research and comparison of the obtained callus with the biomass of natural plant will be conducted.

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Synthesis Of Composites Filled With Modified Hydroxyapatite And Study Of Their Mechanical Properties

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Abstract – The purpose of this work was to increase the compatibility of composite components by modifying the surface of hydroxyapatite particles. Oleic acid and peroxide copolymer VEP-MA were used as modifiers. It was shown that modified composites have higher impact viscosity and tensile strengths.

Keywords – modification, hydroxyapatite, composite.

Introduction

Dispersed hydroxyapatite (HAP) has a very high biocompatibility and capable of interacting with bone tissues, but has a low mechanical strength. Therefore, we cannot use it as a bone substitute. The good solution to this problem is use polymer composite materials based on HAP. However, this is complicated because of the significant difference in surface energy, and hence the poor compatibility of the components. One of the ways to improve the compatibility of composite components is modify the surface of the filler particles. To solve this problem, we used next modifier: oleic acid (OA) and peroxide copolymer VEP-MA to modify the surface of hydroxyapatite.

Synthesis of hydroxyapatite passed through the reaction:

$$10CaCl_2 + 6\,(NH_4)_3PO_4 + 2NH_4OH = Ca_{10}(PO4)_6(OH)_2 + 20NH_4Cl$$

Modification of mineral filler and VEP-MA was carried out in a solution of organic solvent (ethyl acetate), within 2 hours. Upon completion of the modification, the filler was filtered and dried at room temperature to constant weight.

The polyacrylamide-based composite was prepared as follows: an aqueous solution of acrylamide was prepared, dispersed HAP (modified with oleic acid) added to the solution, polymerized acrylamide at 60 °C in the presence of HAP and initiator of potassium peroxide sulfate, the resulting composite was dried to constant mass.

The polyethylene composite was prepared as follows: a mechanical mixture of crushed polyethylene and disperse hydroxyapatite was made, the mixture was filled into a mold and sintered at 180 °C for 4 hours and then remained pressed to a constant temperature. To characterize the composites obtained, studies were carried out on thermomechanical properties, shock viscosity and tensile strength.

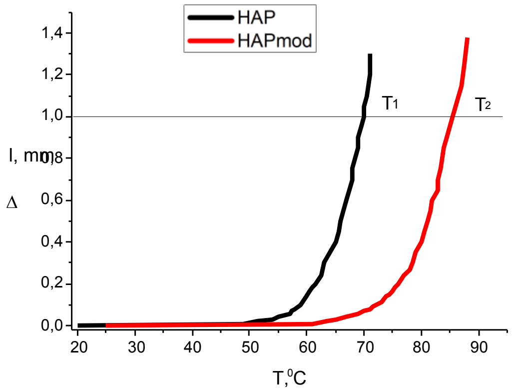

Fig.1. Thermomechanical curves of composites based on polyacrylamide filled with HAP (degree of filling = 40% by mass) and HAP (degree of filling = 40% by mass) modified with oleic acid (degree of modification = 2% by mass), T1 = 700C T2 = 850C.

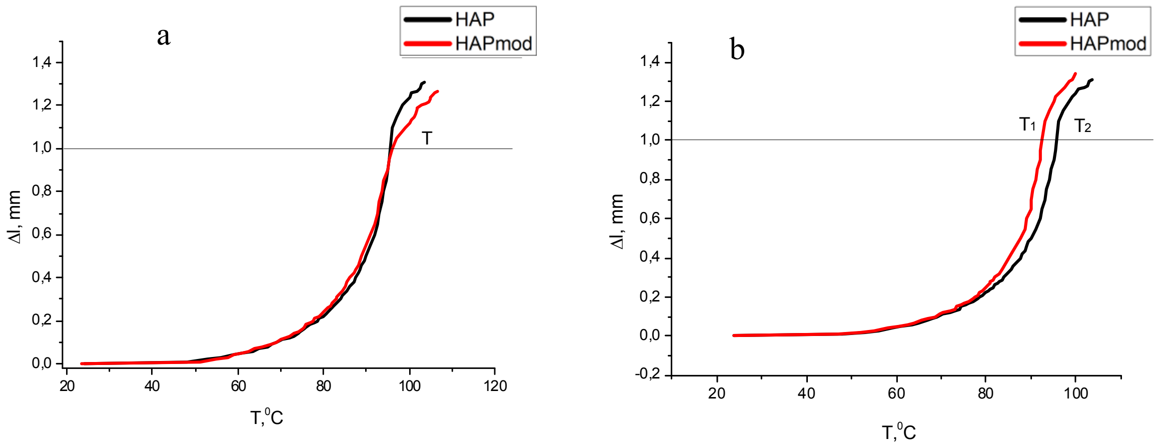

Fig.2. Thermomechanical curves of composite polyethylene filled with HAP ((degree of filling = 40% by mass): a) HAP which modified oleic acid (degree of modification = 2% by mass) T = 97 °C; b) VEP-MA (degree of modification = 2% by mass) T1 = 920C, T2 = 960C

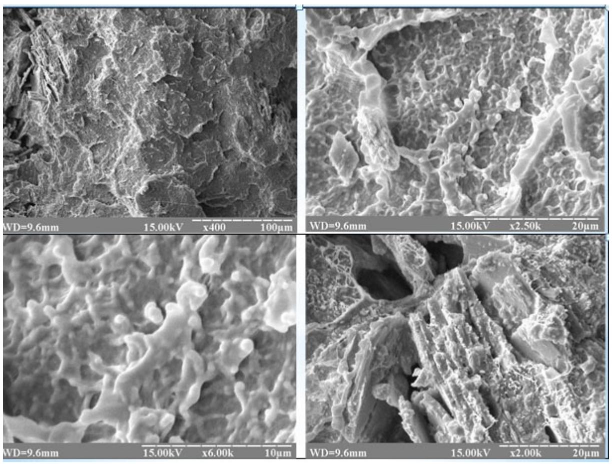

Fig.3. Microphotographs of the fracture surface of a HAP-filled polyethylene composite (degree of filling = 20% by mass) which modified with oleic acid (degree of modification = 2% by mass).

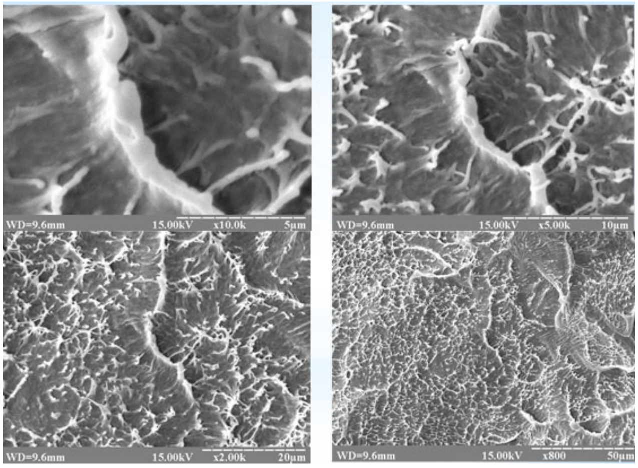

Fig. 4. Microphotographs of the fracture surface of a HAP-filled polyethylene composite (degree of filling = 20% by mass) which modified VEP-MA (degree of modification = 2% by mass)

Conclusion

As a result of the conducted studies it was shown that the modification of hydroxyapatite with oleic acid (degree of modification 1% and 2% by mass) and peroxide modifier (degree of modification = 2% by mass) increases the mechanical properties of the composites obtained. Composites based on polyacrylamide filled with HAP (modified with oleic acid) have an increase of 30% impact strength and an increase in temperature of 20 °C. Polyethylene samples filled modified HAP (OA and VEP-MA) showed no significant changes in thermo-mechanical properties. At the same time, they demonstrated a significant increase (> 65%) of the tensile strength for composites which modified by 1% OA by mass, (>50%) for composites which modified by 2% VEP-MA by mass and (> 30%) for composites which modified by 2% OA by mass.

GREEN CHEMISTRY

Ionic Liquids – Application Driven Synthesis In Green Chemistry

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Abstract* – *Ionic liquid-based strategies are presented as a generic approach to tailoring catalysts as a replacement of hazardous acids in industrially-relevant reactions, to generate both environmentally and economically sustainable processes. The possibilities of application of new bronsted and Lewis acidic ionic liquids as catalysts, mainly in the synthesis of fine chemicals: lactones, amides, esters, Diels-Alder cycloadducts and alkilobenzenes are presented.

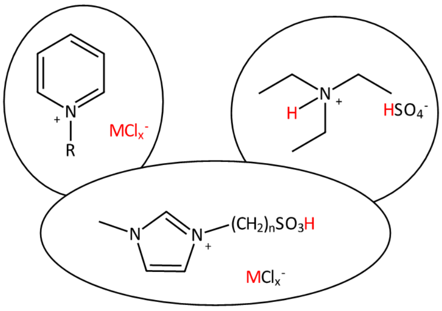
Keywords – acidic ionic liquids, fine chemicals, green chemistry, oxidation, esterification.

Introduction

Searching for new, highly specialized catalysts is a challenge facing modern industry. They are required for the design of clean, environmentally friendly technologies dedicated to the chemical industry. Acidic ionic liquids make promising alternatives to conventional acids for catalysis, and lead to a both greener and economically viable process. In this contribution, various approaches to implementing Brønsted and Lewis acidic ionic liquids as solvents and catalysts in various chemical reactions are discussed. Both homogenous and heterogeneous systems are proposed. Ionic liquids presented in this study are known as "tailor-made." This means that for a specific application, the required catalyst properties can be determined based on an optimal structure by selecting the appropriate reagents for its synthesis.

Results and Disscution

Acidic ionic liquids are salts that may have an acidity centre located in the cation or anion. Examples of acidic ionic liquids structures are presented in Scheme 1.

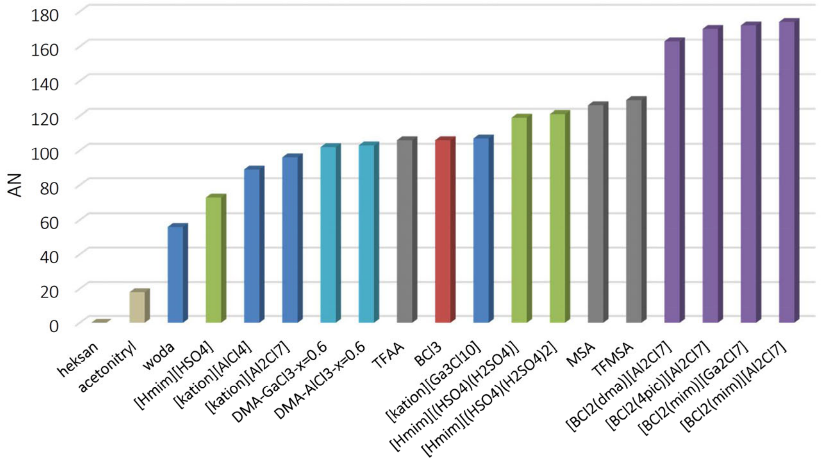


Scheme 1. Acidic ionic liquids with Lewis, Brønsted or both acidity (where M is metal).

The new catalytic systems proposed in this subject include the following:

- protonic ionic liquids based on aliphatic and aromatic amines and sulfuric acid,[1]
- chlorometallate ionic liquids made from dialkylimidazolium cation and chlorometallate anions (metal: Al(III) or Ga(III)), also immobilized on the surface of a mesoporous silica material with a hierarchical pore structure,[2,3]
- borenium ionic liquids based on borenium cation and chlorometallate anions (metal: Al(III), Ga(III)),[4] and
- liquid coordination complexes based on selected amines and phosphines and $GaCl_3$.[5]

Studied catalysts were characterized by spectroscopic methods and their Gutmann Acceptor Numbers (AN) were determined. Thanks to these studies, all acidic ionic liquids, i.e., with properties of both Brønsted and Lewis acids, can be compared and sorted with increasing acidity (Scheme 2).



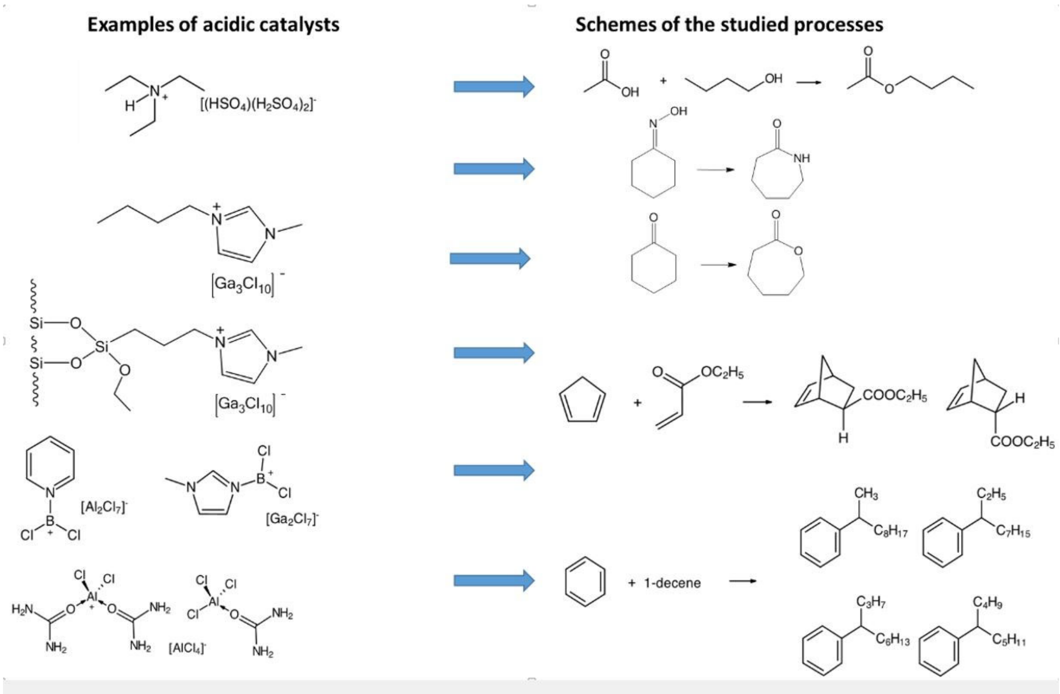
Scheme 2. Comparison of AN for ionic liquids (green – protonic ionic liquids, purple – borenium ionic liquids) and liquid coordination complexes (turquoise) with literature data (abbreviations: TFAA - trifluoroacetic acid, MSA - methanesulfonic acid, TFMSA - trifluoromethanesulfonic acid, $[Hmim]^+$ –1-metylimidazolium cation, DMA – N,N- dimethylacetamide).

The determination of AN has enabled the placement of new acidic ionic liquids in a number of acidic catalysts. The rapid selection of suitable acidic catalysts with appropriate acidity for the reaction is now possible. Borenium ionic liquids exhibit very high acidity, and the highest ever recorded was AN≈182. They are superacids with acidity centres located in both borenium cations and chlorometallate anions. Protonic ionic liquids with a composition $\chi H_2SO_4 = 0.75$ show a strong acidic nature (AN≈121) that is close to methanesulfonic acid (AN = 126.1) and higher than trifluoroacetic acid (AN = 105.5).

Notably, the catalysts were used in homo- or heterogeneous systems. Protonic ionic liquids based on sulfuric acid that were used in the esterification reaction formed a heterogeneous two-phase system with a liquid catalyst. Chlorometallate ionic liquids immobilized on the silica surface used for the Diels-Alder reaction are also examples of heterogeneous catalysts. Borenium ionic liquids in Diels-Alder cycloaddition and chlorometallate ionic liquids in Baeyer-Villiger reaction ensured the homogeneity of the reaction system; similar action was shown with liquid coordination complexes in the Friedel-Crafts alkylation.

To summarize, all of the newly developed ionic liquids were highly active acidic catalysts. Protonic ionic liquids based on sulfuric acid showed significantly higher catalytic activity in the esterification and Beckmann rearrangement reaction than previously described in the literature ionic liquids. Borenium ionic liquids have shown the highest catalytic activity in the Diels-Alder reaction among all systems studied to date. The cost of the synthesis of such a catalyst is high, and the catalyst is consumed during the reaction, but its high cost can be compensated by the very low amount necessary for the reaction. Chlorometallate ionic liquids, also in the form immobilized on a silica surface, exhibit high catalytic activity in Baeyer-Villiger and Diels-Alder reactions. The liquid coordination complexes used in the alkylation of benzene with 1-decene exhibit better results compared to industrial processes and chlorometallate ionic liquids.

All the catalysts listed above are acidic ionic liquids, except the $GaCl_3$-based liquid coordination complexes, which have similar properties to ionic liquids. Spectroscopic studies have shown that they are composed of a mixture of cations, anions and molecules in dynamic balance. Hence, they cannot be completely classified as a group of ionic liquids, which, by definition, are built exclusively from ions.



Scheme 3. Examples of acidic catalysts and their use in the selected reactions.

Conclusion

The ability to select acidity from a rich palette of ionic liquids with Brønsted and/or Lewis properties, a lack of vapour pressure, the ability to create biphasic systems, the ability to effectively separate products from ionic liquid, and the reuse of ionic liquids are the advantages of ionic liquids as acidic catalysts demonstrated in this project.

Acknowledgments

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Researching Of Secondary Metabolites Of Adonis Vernalis

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The Adonis vernalis callus biomass was obtained in vitro using biotechnological method. Secondary metabolites were found in biomass extracts. The results of thin-layer chromatography and spectrometric analysis of Adonis vernalis extracts are indicated. Obtaining of secondary metabolites is promising for the pharmaceutical and cosmetic industry.

Keywords: secondary metabolites, alternative methods of obtaining, callus biomass, Adonis vernalis, cultivation.

Introduction

Currently, it is relevant to search for new biologically active compounds and alternative methods for their obtaining. Valuable sources are vegetable raw materials and products of its processing. The value is determined by the content of both primary and secondary metabolites, in particular alkaloids, glycosides, tannins, saponins, phenolic compounds, vitamins, etc. Most of these substances are difficult to synthesize because they have a complex chemical structure, so the only place of location of biologically active substances is higher plants. The high consumer effect of drugs containing compounds of natural origin is caused by many advantages as low toxicity, high efficacy, low side effects, and the presence of secondary metabolites. The raw material base for obtaining these compounds is the natural resources of medicinal plants. Currently, the arsenal of medicinal plant material is limited, because anthropogenic influences are rapidly increasing, climatic conditions are changing and these greatly affect the biological features of the plants. Modern biotechnology methods offer solutions to the problem by obtaining biomass in vitro, as an alternative source of secondary metabolites. This method has many advantages: biomass grows under controlled conditions, is environmentally friendly, the method does not depend on climatic conditions, so biomass can accrue faster and year-round.

The medicinal plant Adonis vernalis has a special value as a source of secondary metabolites. This plant is threatened with extinction, so the use of the biotechnological method for the obtaining of callus biomass is appropriate and promising.

Adonis vernalis has high cardiological activity due to its content of cardiac glycosides (cymarin, K-strophanthin -β), coumarins. It also contains saponins, benzoquinones, flavonoids, organic acids, steroidal saponins, ascorbic acid, provitamin A, micro and macro elements.

The aim of the study

Determination of the qualitative and quantitative content of secondary metabolites in the obtained Adonis vernalis callus mass.

Materials and methods of research

The seeds of Adonis vernalis were used as raw materials to obtain explants in vitro. Seeds selected after flowering from natural germination location (Lviv region, Ukraine). Seeds were pre-stratified and sterilized with various agents (hydrogen peroxide (96%), sodium hypochloride

(3%)) for further cultivation. The Murashige and Skoog (MS) medium was used for the introduction into the culture of the seeds without phytohormones.

The Murashige and Skoog medium was used to cultivate Adonis vernalis. This medium contains the necessary components for cultivation of explants [1]. Determination of callus biomass was carried out using a weight method. Identification and quantitative determination of the content of secondary metabolites in the obtained callus biomass was carried out in accordance with the methods used for plant material in accordance with the requirements of the State Pharmacopoeia of Ukraine.

At the first stage the content of cardiac glycosides in callus biomass was determined using specific reactions, thin-layer chromatography, commonly used methods of researching [2]. Thin-layer chromatography (TLC) was carried out on plates of the Scornful brand, 10 × 10 cm in size. Ethyl acetate-methanol was selected as the solvent system - water in ratio of 75: 10: 7.5.

Content of the sum of polyphenols, tannins, flavonoids was determined spectrophotometrically in terms of pyrogallol, rutin, pyrogallol [3].

Results

As a result of the research were selected the optimal conditions for induction of Calusogenesis Adonis vernalis, namely, the medium of MS with the corresponding phytohormones (IOC, NOC, kinetin), illumination 4000lk at a 16 hour photoperiod at a temperature of 22-25 °C and optimal cultivation time is 40 days. It has been established that the maximum biomass increase is 3.04 grams of dry matter per 100 ml of nutrient medium at 40 days of cultivation. The obtaining high-quality callus biomass was used for further research.

Qualitative analysis of the content of biologically active compounds in the callus biomass identified the presence of glycosides, flavonoids, tannins and polyphenols.

As a result of conducting TLC was identified cardiac glycosides (cymarin, strophanthin - β); phenolic compounds (gallic acid, myrethecin, (+) epicatechin, 3,4-hydroxybenzoic acid).

The quantitative content of the amount of polyphenols in the Adonis vernalis callus biomass is 2.31%, the amount of flavonoids is 2.04%, tannins - 0.83%.

Conclusions

The callus biomass of Adonis vernalis was obtained and its ability to prolong the growth and accumulation of secondary metabolites as cardiac glycosides, tannins, flavonoids and polyphenols was established.

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Epoxy Composites Based On Cyclic Carbonates Of Vegetable Oils

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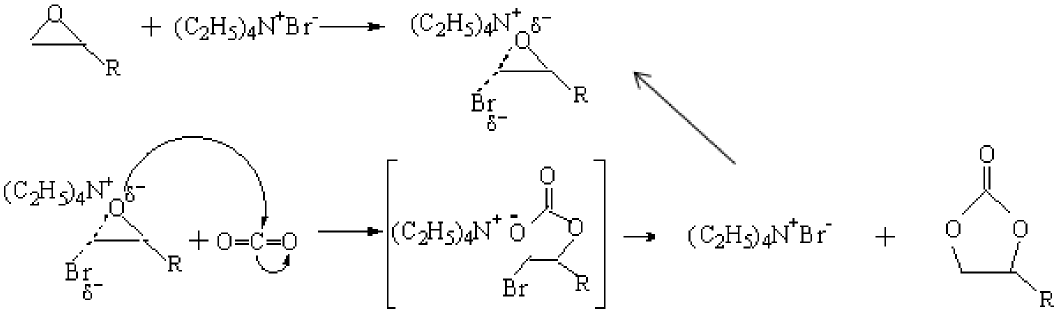
One of the most prospective is Non-isocyanate polyurethane synthetic pathway method is the interaction of carbonized vegetable oils (CVO) and amines of different chemical nature that prevent using highly toxic isocyanates. The polymeric composite materials based on amine modifiers and epoxy resins were obtained. The physical-mechanical properties of the polymeric materials modified with amines were determined.

Keywords – cyclocarbonated vegetable oils, soy and linseed oils, epoxy-cyclocarbonate systems, aliphatic-diethylenetriamine, non- isocyanates

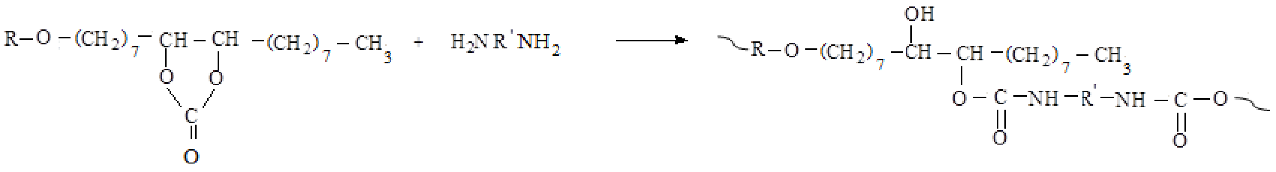
Introduction

Green chemistry of polyurethanes is a new promising direction of polymer chemistry and many problems in this area are still waiting for their solution. Oligomers with cyclic carbonate groups are synthesized from epoxy-containing substances. At the same time, the most perspective is the catalytic reaction of CO2 with epoxides. It is known that functionalized vegetable oils can be used as binding agents for polymer composites.

In this work carbonized vegetable oils (CVO) with five-membered cyclocarbonate groups in their structure were synthesized. Soy (CC SO) and linseed oils (CC LO) were used in the synthesis. The optimal conditions for the synthesis of oligocyclic carbonates (OCCs) such as type and concentration of catalyst, temperature and reaction time were determined.



Polyurethanes were obtained (the scheme is shown below) from carbonized vegetable oils and various amine structures, without application of isocyanates:



The OCCs which can be mixed unlimitedly with epoxide resin (EC) DER331 were used in modification of epoxy composites. Two methods of epoxy-cyclocarbonate systems hardening were tried in this work. In one-stage method (simultaneous mixing of all components) polyamine hardeners were added. In two-stage method the preliminary preparation of urethane amine and subsequent hardening of the epoxy oligomer were used. The kinetics of the hardening of CC SO epoxides were studied by FTIR spectroscopy.

Table 1

Properties of epoxy composites modified by epoxidized cyclocarbonated soybean oil (CC SO).

N	Epoxy composites	Tensile strength, MПa	Elongation ,%	Tg, 0C	Impact viscosity J /m2
1	DER331+ DETA	16	0.6	93	14.1
2	(95% DER331+5% CC SO)+ DETA	34	5.7	91	15.0
3	(90% DER331+10% CC SO)+ DETA	45	6	87	14.7
4	(80% DER331+20% CC SO)+ DETA	57	9	57	20.8
5	(70% DER331+30% CC SO)+ DETA	51	12	56	26.6
6	(60% DER331+40% CC SO)+ DETA	42	9	53	28.6

It is shown that modification of CC SO epoxides leads to a significant increase in tensile strength and elongation of samples (Table 1). The dependence of tensile strength and compressive strength of polymers on the ratio of the EC and the CC SO has an extreme behaviour for the investigated amines. A significant increase in the impact strength of composites (impact fracture toughness increases for some systems by 6-8 times) is common to all amines (aliphatic-diethylenetriamine (DETA), alicyclic, aminoacids, polyamides).

Conclusion

Changing the types of amine curing agent gives possibility to change the kinetics, mechanical and technological properties of epoxy composites. Modification of epoxy CVO leads to decrease of glass transition temperature (Tg). Significant decrease in Tg is observed for specimens which contain from 20 to 40% of CC SO.

Synthesis and antibacterial activity of novel 3-substituted 1-(2-methyl-5-nitrophenyl)-5-oxopyrrolidine derivatives

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Abstract* – *The synthesis of novel azole derivatives has been accomplished during chemical transformations of the 1-(2-methyl-5-nitrophenyl)-5-oxopyrrolidine-3-carbohydrazide. The structure of the synthesized compounds was determined by NMR and IR spectroscopies. Most of the synthesized compounds were screened for their antibacterial activity against S. aureus, L. monocytogenes, E. coli, and P. aeruginosa bacteria strains.

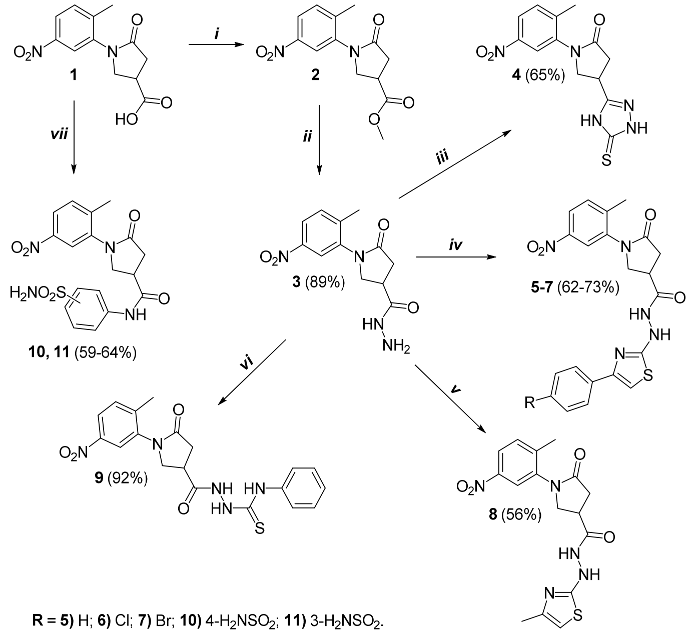
Keywords – pyrrolidin-2-ones, thiazoles, sulphonylamides, antibacterial activity.

Introduction

Pyrrolidinone derivatives are widely known for their biological activities such as antimicrobial [1], antiviral [2], etc. Furthermore, thiazole is an important pharmacophore associated with varied biological activities including antimicrobial [3], antiviral [4]. In the view of this interesting pharmacological content we have decided to design and synthesize the molecular framework of new pyrrolidinone derivatives with heterocyclic or acyclic fragments and investigate their antibacterial activity.

Results and discussion

Chemistry



i) methanol, H_2SO_4, reflux, 8 h; ***ii)*** $N_2H_4 \cdot H_2O$, propan-2-ol, 5 h, reflux; ***iii)*** KSCN, 30% acetic acid, reflux, 48 h; ***iv)*** 1-(4-Substituted phenyl)-2-thiocyanatoethan-1-one, 1,4-dioxane, reflux, 72 h; ***v)*** 1-thiocyanatopropan-2-one, 1,4-dioxane, reflux, 48 h; ***vi)*** phenyl isothiocyanate, methanol, rt, 8 h; ***vii)*** benzenesulfonamide, 160 °C, 4 h.

Scheme 1. Synthesis of 1,3-disubstituted 5-oxopyrrolidines 2–11.

1-(2-Methyl-5-nitrophenyl)-5-oxopyrrolidine-3-carbohydrazide (3) was prepared from carboxylic acid 1 via esterification reaction with methanol in the presence of sulphuric acid as a catalyst which resulted in formation of methyl ester 2 (Scheme 1). Finally, the subsequent reaction of the ester 2 with hydrazine monohydrate was carried out providing hydrazide 3. 1,2,4-Triazole-5-thione 4 was obtained by the reaction of hydrazide 3 and KSCN in 30% acetic acid. Corresponding 2,4-disubstituted-1,3-thiazoles 5–8 were synthesized by the reaction of respective thiocyanatoethan-1-ones or 1-thiocyanatopropan-2-one with hydrazide 3 in dry 1,4-dioxane. Thiosemicarbazide 9 was obtained from the reaction of hydrazide 3 and phenylisothiocyonate in good yield (Scheme 1). Sulphanilamides

10, **11** were synthesized by heating 1-(2-methyl-5-nitrophenyl)-5-oxopyrrolidine-3-carboxylic acid (**1**) with corresponding benzenesulfonamides.

Biology

The antimicrobial activity of the compounds 4–11 was screened by testing their different concentrations against the Gram-positive cocci Staphylococcus aureus and Gram-negative rods Escherichia coli, Pseudomonas aeruginosa, and Listeria monocytogenes using the broth and spread-plate methods. The minimum inhibition concentration (MIC, μg/ml) and the minimum bactericidal concentration (MBC, μg/ml) values are presented in Table 1. A broad-spectrum antibiotic oxytetracycline was used as a positive control.

Table 1

Minimum inhibitory concentration (MIC) and minimum bactericidal concentration (MBC) values for the tested compounds

Compound	S. aureus		E.coli		P. aeruginosa		L. monocytogenes	
	MIC, μg/ml	MBC, μg/ml	MIC, μg/ml	MBC, μg/ml	MIC, μg/ml	MBC, μg/ml	MIC, μg/ml	MBC, μg/ml
9	250	250	250	250	250	250	250	250
10	15,6	31,25	15,6	15,6	15,6	15,6	31,25	31,25
11	15,6	31,25	15,6	15,6	7,8	7,8	15,6	15,6
C*	62,5	62,5	250	250	250	250	62,5	62,5

*Oxytetracycline was used as a control for *S. aureus, E. coli*, *P. aeruginosa*, and *L. monocytogenes*.

Compounds 5–8 possessed moderate antibacterial activity against the tested bacterial strains. Thiosemicarbazide 9 exhibited the same antibacterial activity against E. coli and P. aeruginosa as the control sample. Sulphanilamides 10, 11 have showed an exceptional antibacterial activity.

Conclusion

A series of 5-oxopyrrolidine derivatives containing functionalized azole or acyclic fragments were synthesized. Most of the obtained structures were tested for their antibacterial properties and exhibited moderate biological activity. However, the results of sulphanilamides 10, 11 antimicrobial screening showed that their antibacterial properties were better than broad-spectrum antibiotic oxytetracycline, which was used as a positive control.

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Synthesis and antimicrobial activity of novel 2,4-disubstituted thiazoles

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Abstract* – *A beneficial modifications of 2-substituted thiazoles by incorporating different functional groups into the structure such as carboxyl, chloromethyl, (phenylamino)methyl, ethoxyoxoethyl, which determine a certain chemical reactions of the compound was developed. All the synthesized compounds were tested for their in vitro antimicrobial and antifungal activity.

Keywords – amino acids, antimicrobial agents, cyclization, functionalized thiazoles, reactive intermediates.

Introduction

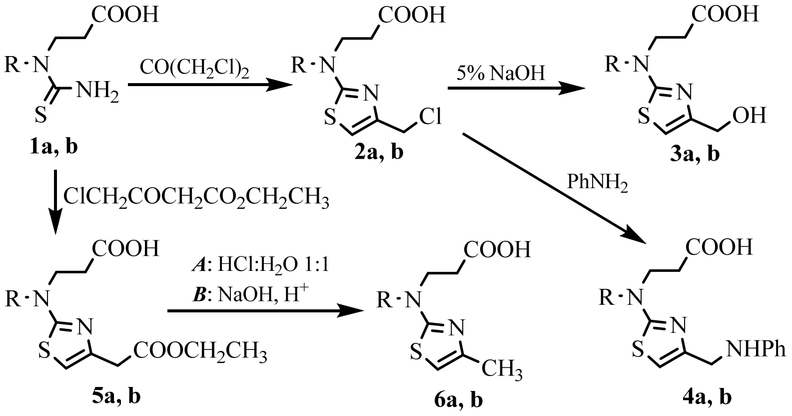
A large number of chemotherapeutics are developed for medicinal use in nowadays but the increasing resistance of pathogens to available pharmaceuticals has created an essential demand for new efficient classes of antimicrobial agents. A unique small-ring heterocycle – thiazole containing nitrogen and sulphur atoms, play an important role in medicinal chemistry and is widely used in the development of bioactive compounds, drugs, as well as industrial products [1, 2]. Thiazole derivatives are associated with a broad spectrum of biological properties, including antimicrobial [3], antituberculous [4] and anticancer [5]. The aim of this work was to synthesize functionalized thiazoles with reactive functional groups that could be intermediates for the synthesis of variously functionalized thiazoles.

Results and discussion

Chemistry

Our initial aim of this work was to synthesize a series of disubstituted aminothiazoles (Scheme 1). To give the derivatives 2**a**, b the reaction of the corresponding thioureido acids 1**a**, **b** with 1,3-dichloroacetone was carried out under reflux in acetone for 2 **h**. Under alkaline hydrolysis conditions, the chloromethyl group of compounds 2**a**, **b** was replaced by a hydroxymethyl fragment 3**a**, **b**.

Scheme 1. Synthesis of disubstituted thiazoles **2–6**



a R = naphthalen-1-yl; **b** R = *p*-tolyl

The interaction of aminothiazoles **2a, b** with aniline in dimethylformamide results in the formation of the corresponding 3-(naphthalen-1-yl(4-((phenylamino)methyl)thiazol-2-yl)amino)propanoic acid **(4a)** and 3-((4-((phenylamino)methyl)thiazol-2-yl)(*p*-tolyl)amino)propanoic acid **(4b)**. Esters **5a, b** were prepared by the reaction of corresponding thioureido acid **1a, b** and ethyl 4-chloroacetoacetate in acetone. The attempts of the acidic or alkaline hydrolysis of the ethoxy oxoethyl moiety in **5a, b** did not succeed and led to the unexpected products 4-methylthiazole derivatives **6a, b**.

Biology

All synthesized compounds **2–5** were tested against bacteria strain *Staphylococcus aureus* 209-P and fungi strains *Candida tenuis* VCM Y-70, and *Aspergillus niger* VCM F-1119 for their *in vitro* antimicrobial activity by the diffusion method in agar and the serial dilution method. Analysis of the structure-activity relationship of the synthesized compounds has revealed that derivatives with *p*-tolyl moiety are more active than naphthalenyl analogues. Majority of the most active compounds against *C. tenuis* identified by the serial dilution method are the ones bearing *p*-tolyl fragment. Compounds **3b–5b** showed equal effectiveness as Nystatin. In the case of *A. niger*, the most active appeared to be compounds containing *p*-tolyl moiety, i.e. derivatives **2b**, **4b** and **5b**. The advantage of compounds with the *p*-tolyl moiety has been also demonstrated by antibacterial activity of **3b** against *S.aureus*, the MIC of which corresponds to the control Vancomycin.

Conclusion

In summary, using different types of chemical reactions we have synthesized a series of thiazoles with reactive functional groups in the molecule, which allow predicting, design and formation of new thiazole structures.

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Chromatographic studies of extractant residues in the chemical technology of carotenoid production

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Selected parameters of gas chromatographic analysis, which allow to determine and control the purity of industrial carotene preparations for nutrition and medicine purpose. It has been discovered that undesirable accumulation of chemical reagents in carotenoids in the course of a multi-stage and long- term biomaterial extraction mode requires additional purification from the residues of dangerous extractants.

Key words: chemical technology, carotenoids, gas chromatographic analysis, chemical extractants, toxicant residues

Problem analysis

Industrial forms of carotenoids have a wide range of applications in the fields of medicine and nutrition that are related to human health. These are nutritional supplements (dyes E160c, E160a, E160d); medicinal and pharmaceutical substances; supplements to the diet of animals and birds, components in cosmetology. Therefore, qualitative indicators of carotenoids marketable products are strictly regulated by sanitary-hygienic norms and standards of the State Pharmacopoeia of Ukraine. This approach is aimed at harmonizing the laws of Ukraine "On Medicines"; "On medicinal products" within the framework of regulatory documents of the European Pharmacopoeia, identical to international standards concerning the requirements of ICH, GMP [1, 2]. The rules of the above-mentioned documents are focused on the safe level of purity of medicinal and nutrition products and other types of products. They provide for control and regulation of the content of residual quantities of chemical extractants using validated analytical methods. In this aspect, the solution to the problem of the selection of highly effective sensitive methods for detecting and controlling the level of harmful substances (in particular, organic volatile chemical compounds) in vital nutrition and medicinal substances is up-to-the-minute. Among the modern analytical methods, various types of chromatographic analysis are recognized as such [3, 4].

It is known that plant products include a group of yellow-orange liposoluble pigments – different carotenoid isomers (β-carotene, lycopene, lutein, zeaxanthin, etc.). The latter are components of plants (algae cells, herbs, shrubs, trees, many fruits and vegetables) and fungi. The biological activity of carotenoids occurs in many life processes: light and color perception, in antioxidant, immune stimulating, protect against cancer and adaptogenic actions, participation in regulation of differentiation and reproduction of cells, etc.

The structure of carotenoid molecules, in which structural isoprene units are interconnected in a long chain, determines their ability to transform enzymatically in the body of human and many animals into the retinal molecules (the precursor of vitamin A). This transformation mechanism determines the value of carotenoids as products for the nutrition, medical, pharmacological and other industrial sectors.

Carotenoids are synthesized by chemical and microbiological ways (based on bacterial cells, actinomycetes, yeast, filamentous fungi). At the same time, the most promising source of carotenoid pigments is the strain of mucorales heterothallic fungi Blakeslea trispora, capable of carotenogenesis through the course of complex enzymatic reactions in multicomponent nutrient media. To extract carotenoids from mycelial biomass, both pure organic solvents (hexane, acetone, methanol, propanol, methyl ethyl ketone, ethyl acetate, methylene chloride) and solvent mixtures – acetone: carbon tetrachloride (2-10 : 1); n-hexane: acetone (175 :5), petroleum ether: tetrahydrofuran (4 : 1), chloroform: methanol (2 : 1) are used, and also vegetable oils for direct extraction from vegetable raw materials (carrot, pumpkin, sea buckthorn, alfalfa, etc.).

Carotenoids of industrial biotechnological preparations based on Blacheslea trispora are represented by 90% of β-carotene and 10% by 10 % – α-, γ-carotenes and lycopene.

Given that the mode of extraction of these carotenoids by chemical agents from fungi biomass is a multi-stage and long process, and for the manufacture of nutrition, pharmacopoeial and medical preparations, this technology requires additional purification of carotenoids with organic solvents [3], undesirable accumulation of the latter in the target substance is possible.

The purpose of the study is to develop a method for determining and conducting a quantitative analysis of toxicant residues – organic extractants of chemical nature using an accurate, sensitive analytical method, aimed at reducing environmental risks by improving the purity and quality of products for nutrition and prophylactic purposes.

Study results

As objects of research, industrial forms of dietary supplements were selected: β-carotene (E160a), lycopene (E160d), β -carotene oil and water soluble β-carotene, obtained by microbiological synthesis from fungi biomass of Blakeslea trispora. In a role of extractant, manufacturer used methylene chloride solvent stabilized with methanol.

According to the requirements of ICH on the toxicity of organic solvents in medicinal products, methylene chloride and methanol belong to 2nd class of hazard [1, 2]. Methylene chloride is characterized by a narcotic effect, reaction of irritation of the mucous membranes of the eyes and respiratory organs, prolonged exposure destroys the liver, nervous and cardiovascular systems. Therefore, the content of methylene chloride in carotenoids should not exceed 0.03%.

We investigated the direct gas chromatographic analysis of liquid and solutions of solid industrial forms of carotenoids. Assessment of the suitability as a solvent of a wide range of various chemical nature liquid substances (hydrocarbon aliphatic, aromatic, alcohols, ketones, esters) was carried out. The vast majority of investigated substances contain volatile impurities that appear on the chromatogram in the area of methylene chloride and prevent its quantitative determination. It has been found that the most suitable as a solvent for industrial forms of carotenoids can only be paraxylene and ethylbenzene.

The need to determine residual amounts of methylene chloride in carotenoid type biological preparations at the level of the requirements of international standards [1] requires the operation of a chromatographic detector in the most sensitive mode. This regulates stringent requirements for the thermal stability of the stationary phases of the separation system.

It has been established that among a wide range of stationary phases of different chromatographic polarity, only methyl and methylphenylsiloxanes correspond to this criterion.

The method of adding a reference to the analyte is most reliable in gas chromatography. The reference substance shall meet the following requirements:

– peak of the reference should appear on the chromatogram near the peak of methylene chloride;

– there should be a complete separation of the reference and methylene chloride peaks; reference should not contain impurities whose peaks coincide or are poorly separated from the peak of methylene chloride.

It has been found that these requirements are mostly consistent with isobutanol. Solutions of known concentrations of isobutanol and methylene chloride in paraxylene were used to determine the calibration factor. Subsequently, a solution of isobutanol was added to the solution of the industrial form of carotenoid and the content of methylene chloride was determined using the determined calibration factor.

Studies were performed on a chromatograph with a flame ionization detector.

Separation system:

- 3 m long column with an internal diameter of 3 mm;
- 5% OV-17 sorbent on N-super-chromatone 0.16-0.20 mm;
- sample volume 0.4– 0.6 μl;
- column temperature 70°C;
- sample evaporation temperature 200°C.

Determination of residual amounts of methylene chloride in carotenoids was carried out in four-, fivefold repeatability.

Results of statistical processing of the determination of methylene chloride content in some industrial samples of carotenoids are given in Tables 1 and 2.

Table 1

Results of statistical processing of the determination of methylene chloride content in an industrial sample of *β*-carotene (P = 0,95; n = 5)

Measured concentration, %	Average value (x±5), %	Permissible content, %
0,167	0,167±0,006	0,03
0,168		
0,162		
0,163		
0,173		

Table 2

Results of statistical processing of the determination of methylene chloride content in an industrial sample of lycopene (P = 0,95; n = 4)

Measured concentration, %	Average value (x±5), %	Permissible content, %
0,115	0,111±0,004	0,03
0,112		
0,109		
0,110		
0,111		

Obtained results indicate that the residual amount of methylene chloride in the в-carotene sample was 0,167%, which exceeds the permissible concentration according to ICH requirements by 5,6 times, and the residual amount of methylene chloride in the lycopene sample was 0,111%, which exceeds the permissible concentration in accordance with the requirements of the standard by 3,7 times.

Conclusions

Thus, the gas chromatographic analysis method developed by us makes it possible to effectively control the residual amount of extractant in carotenoids for both nutrition and medicinal purposes preparations, and the technology of their production requires additional purification from residues of hazardous chemical extractants.

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Polyurethane Foams With Reduced Flammability Based On Oligoetherols Synthesized From 1,3-Bis(2-Hydroxyethyl)Uracil, Boric Acid And Ethylene Carbonate

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Abstract* – *Polyurethane foams using oligoetherols synthesized from 1,3-bis(2-hydroxyethyl)uracil, boric acid and ethylene carbonate are obtained. Some properties of the foams, such as apparent density, water uptake, dimensions stability, thermal stability, compression strength, thermal conductivity, oxygen index and horizontal burning were investigated. The obtained foams show an improved thermal stability and reduced flammability.

Keywords – 1,3-pyrimidine ring, 1,3-bis(2-hydroxyethyl)uracil, boric acid, ethylene carbonate, oligoetherols, polyurethane foams, improved thermal stability, reduced flammability.

Introduction

The main disadvantages of plastics are low thermal resistance and relatively low decomposition temperature. The thermal resistance of typical polyurethane foams usually does not exceed 120°C, and the degradation of polyurethane foams is accompanied by the formation of flammable substances, which creates a fire hazard. In the course of burning, polyurethanes emit toxic gases, among others hydrogen cyanide, carbon monoxide and carbon dioxide, and nitrogen oxides. This is a danger to human life and health, and for this reason methods to reduce the flammability of polyurethane foams and improve their thermal resistance are sought. Foams of improved thermal stability can be obtained by using a polyetherols component containing some heterocyclic rings, e.g., 1,3-pyrimidine [1-3]. Unfortunately, they are flammable. Flammability can be reduced by incorporating organic compounds with boron atoms [4, 5].

Results and Discussion

The syntheses of polyurethane foams based on oligoetherols with a 1,3-pyrimidine ring and boron atoms has been proposed. Syntheses the oligoetherols were carried out in two ways. In the first method 2,4-dioxopyrimidine-1,3-diethanol bis(dihydroborate) in the reaction of 1,3-bis(2-hydroxyethyl)uracil with boric acid was obtained, and next it was then treated with excess of ethylene carbonate in the presence of potassium carbonate. The second method relied on the direct reaction of 1,3-bis(2-hydroxyethyl)uracil with boric acid and ethylene carbonate. The structure of the obtained oligoetherols was determined by instrumental methods (IR, 1H-NMR and MALDI-ToF spectra). The physicochemical and thermal properties of oligoetherols were examined. In the next stage, the obtained oligoetherols as polyol components to prepare polyurethane foams were used. Foaming was carried out in a laboratory scale. The composition of foaming samples was selected experimentally. Polymeric MDI was used as a isocyanate agent, and water was a foaming agent. Triethylamine was used as a catalyst and silicone L-6900 was applied as a surfactant. It has been found that foams with regular, small pores are obtained using 3 wt% of water, 2.7–3.85 wt% of catalyst, 1.95 wt% of surfactant and 140–160 g of isocyanate per 100 g of oligoetherol (Fig. 1).The physical properties of selected polyurethane foams: apparent density, water uptake, dimension stability, compression strength, thermal conductivity coefficient, thermal resistance and flammability of selected polyurethane foams were studied. The apparent density of the foams was in the range of 56.09–91.34 kg/m3, so they are classified as rigid materials. Along with the increase in the content of boron in foams, their apparent density increases. Water absorption after 24 h of exposition was between 8.05–27.62 wt%. Dimensional stability tests show that shrinkage of the foams after 40 h exposure at 150ºC is very small. The thermal conductivity of the obtained materials falls in the range 0.0349–0.0368 [W/(K·m)]. Dynamic thermal analysis shows that 50% weight loss of foams occurs at 299–322°C. Mechanical properties were evaluated on the basis of compression strength measurements. Before the thermal treatment compression strength at 10% deformation strain of the foams was in the range of 0.29–0.33 MPa. It has been observed, that one month long thermal treatment at temperature 150°C resulted in higher compression strength (0.58–1.27 MPa). Flammability of the foams were studied as follows: horizontal burning tests were made and oxygen index was measured. The horizontal burning test shown, that all the resulting foams are self-extinguishing in the air. The oxygen index of the obtained foams has values in the range of 22.0–24.1vol%. The foams with the highest boron content presented the lowest flammability. The flammability tests allow to state that the obtained materials are self-extinguishing and flame-retardant.

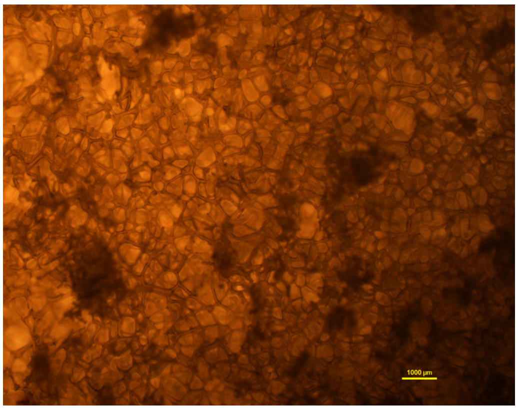

Fig.1. Microscope image of the foam obtained from oligoetherol synthesized from 1 mol 2,4-dioxopyrimidine-1,3-diethanol bis(dihydroborate) and 16 moles ethylene carbonate.

Conclusion

Polyurethane foams obtained from oligoetherols synthesized from 1,3-bis(2-hydroxyethyl)uracil, boric acid and ethylene carbonate characterized an reduced flammability and improved thermal stability compared to classic, rigid polyurethane foams.

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Properties of biodegradable films based on thermoplastic starch and poly(butylene succinate) with plant oil additives

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The paper presents study of the plant oils effect on the properties of starch/polyester blends. In the first stage of the study thermoplastic starch (TPS) with different amount of oils were prepared. I the second stage TPS materials were blended by extrusion process with commercially available biodegradable polyesters - poly(butylene succinate).

Keywords – thermoplastic starch, poly(butylene succinate), blends, biodegradable films.

Introduction

The growing interest in using eco friendly products has stimulated research and development of new materials such as biodegradable polymers. Furthermore, due to various restrictions regulated by the law and a very high consumption of plastics, fluctuating cost of petroleum-based materials based on oil prices and environment pollution, biodegradable polymers have been developed and have partially or completely replaced conventional plastics in some applications.

Starch is an abundant and naturally occuring polymer that is increasingly used in the production of packaging. Starch has been considered as an attractive biopolymer because of its low cost, low density and biodegradability. It can be used in its native form as a filler with another polymer or it can be processed into a thermoplastic material and mixed with other polymers to forms polymer blends [1, 2].

Native starch is found in granular form and it is composed of two major polysaccharides, amylose and amylopectin (Fig. 1). Linear amylose is soluble in water and has a helical structure. Amylopectin molecules are short, branched and easy to crystallize.

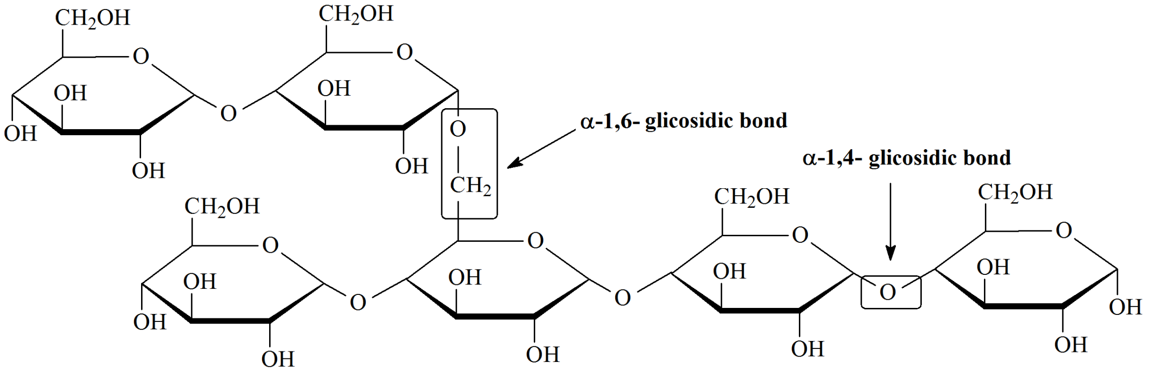

Fig. 1. Chemical structure of starch.

Starch granules exhibit hydrophilic properties and strong itermolecular association via hydrogen bonding due to the hydroxyl groups. The melting point of native starch is higher than the thermal decomposition temperature, hence starch cannot be thermally processed in native form. To resolve this problem, non-volatile plasticizers such as polyol (glycerol, ethylene glycol etc.) are commonly used. For this purpose, the plasticizers is added to starch, and then the material is processed in the extruder at higher temperatures and shear forces. In this way, the crystal structure is destroyed and replaced by starch hydrophilic thermoplastic material with an amorphous structure which can be processed like other thermoplastics by extrusion process. A new material obtained from native starch with plasticizers is called thermoplastic starch (TPS) [3].

Industrial applications of starch based materials are limited by the susceptibility of their final properties to certain environment changes. They present poor mechanical properties and water vapour barrier capacity, compared to synthetic polymers. Thus, blend formation by adding compatible materials represents a promising alternative to improve the final properties reducing the sensitivity to environment parameters like humidity, temperature or radiation exposure. Within this context, the use of a hydrophobic biodegradable polymer such as polylactide (PLA), poly(butylene succinate) (PBS) or poly(□-caprolactone) (PCL) for starch-based blends would offer the possibility of enhancing mechanical behavior and reducing water vapour permeability [4,5].

Poly(butylene succinate) PBS is one of the promising hydrophobic aliphatic polyester (Fig. 2) with many interesting properties including biodegrability, melt processability and thermal and chemical resistance. PBS can be processed in the field of textiles into melt blow, multifilament, flat and split yarn and also in the field plastics into injection molded products. The characteristics of PBS are simililar to those of polyethylene. It has good elongation at break and low melting point with ductile property that can be easily applicable to conventional processing techniques such as extrusion and injection molding.

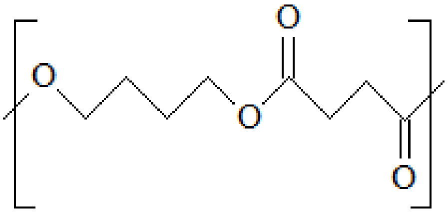

Fig. 2. Chemical structure of poly(butylene succinate).

One of limitaions regarding the use of PBS in various commercial application is its high cost. Blending with low-price resins like thermoplastic starch is an alternative approach to resolve those problems. Hovewer, it was confirmed that TPS/PBS blends were immiscible and have the poor compatibility. Theer are very few reports about TPS/PBS blends and their compatibilization. One of the possibilites is to obtain the reactive PBS. It was found that the mechanical properties of blends improved and reduced water absorption with the increase of the reactive PBS content in blend [6]. Another options to improve properties of hydrophilic-hydrophobic blend is to incorporate the additives that will modify the interfacial properties of the polymers. The compatibilizing additives can be amphiphilic compounds which in their structure have hydrophilic and hydrophobic groups. The most common amphiphilic compounds are fatty acids, lipids, triglycerides, surfactants or proteins [7,8].

The paper presents the study on the influence of the addition of amphiphilic compounds contained in rapeseed oil and blackcurrant seed extract on selected properties of blends and films based on thermoplastic starch (TPS) and poly(butylene succinate) (PBS).

Experimental part

In the first stage of the research, a thermoplastic starch in the granulate form containing various concentrations of rapeseed oil or blackcurrant extract using twin screw co-rotating extruder was obtained. Then, the TPS granulate was blended in extrusion process with commercially available biodegradable polyester - poly(butylene succinate) (PBS). The blend containing 50 wt% of TPS was prepared. In order to determine the properties of obtained polymer granules, water content in granulate, FTIR spectroscopy and melt flow index (MFR) were analysed.

In the second stage of the research, films on a large-scale scale from the prepared materials by extrusion blow molding were obtained. The extrusion processes for individual mixtures were optimized and tests to determine the mechanical properties (tensile strength and elongation at break) of the obtained films were carried out.

Results and disscusion

Water content and melt flow index (MFR)

Determination of water content in biogranulates was carried out by Karl Fischer volumetric titration method at 120°C. The melt mass flow rate (MFR) was measured by using a plastometer CEAST MF20 apparatus at 190°C with 2,16 kg nominal load adapter to the standard ISO 1133.

Table 1.

Results of the water content and mass melt flow index (MFR) of the TPS/PBS

	50% TPS + 50% PBS	
	water content [%]	MFR [g/10min]
without additive	1,6	1,9
0,5% BC	1,9	1,7
1,0% BC	3,6	2,4
1,5% BC	3,5	3,3
0,5% RO	1,5	1,8
1,0% RO	2,4	2,7
1,5% RO	2,5	2,3

The water content in the obtained blends is an important parameter in their further processing. During the production of the film from individual mixtures by blow molding, the effect of water content in the granulate on the structure of the film was observed. On the one hand, the minimum amount of water is necessary for the easier processing, and on the other hand, if the amount of water in the granulate from which the film is extruded is too small, inclusions of starch granules occur. Obtaining the optimum amount of water in the granulate of the blend determines the production of the film without disadvantageous inclusions and with a satisfactory efficiency.

The simplest measurement of the rheological properties of thermoplastic polymers is the determination of the mass or volume melt index of plastics using a plastometer. Knowing the value of the melt flow index of a material, it is possible to select the processing methods.

The following table summarizes the results of the water content and mass melt flow index (MFR) for individual granulates.

The water content in the obtained granules determines the production of a film with good structural properties. The value of the melt flow index (MFR) obtained for individual TPS/PBS granulates enables processing by extrusion blow molding and films production.

FTIR spectroscopy

FTIR spectra were measured using Nicolet iS10 Spectrum Scanner (Thermo Scientific, USA) over the wavenumber ranging from 600 to 4000 cm-1 using ATR-FTIR mode system. Figure 3 shows overlaid FTIR spectra of TPS/PBS and blend with 1.5% oil additive.

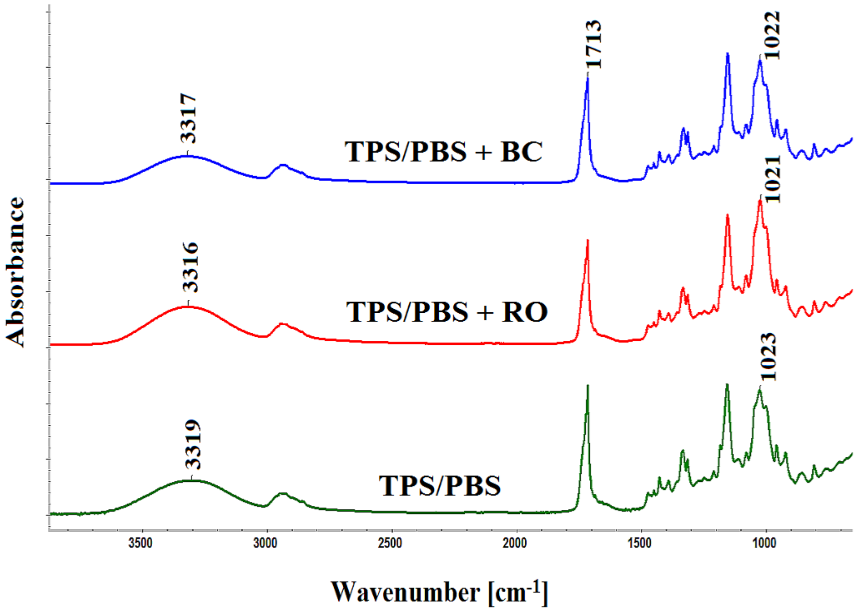

Figure 3. FTIR specta of TPS/PBS blends.

As a result of the addition of 1.5% (BC) or (RO) oils to the TPS/PBS blend, the band at 1020 cm-1 derived from the vibrations of the C-O groups in the glucose ring occurring in the starch structure increases its intensity. This is the effect of interactions between the hydrophobic groups in the oil structure and the chains of the hydrophobic polyester. The C-O groups vibration band in the spectrum of oil-containing blends is shifted from 1023 to 1022 cm-1 (BC) and 1021 cm-1 (RO), confirming the improvement in the miscibility between the hydrophobic PBS polyester and the hydrophilic thermoplastic starch. An increase in the intensity of the hydrogen bond band at about 3300 cm-1 in the TPS/PBS blends containing the oil additive (BC) or (RO) and its shift towards the lower wavenumbers was also observed. This is due to the fact that the carbonyl group C=O present in the oil compounds structure forms additional hydrogen bonds with the hydroxyl groups of the starch.

Mechanical properties

The mechanical properties of the materials were determined using a universal testing machine Instron 3340 according to the ISO 527 standard. Figure 4 shows the dependence of the tensile strength and elongation at break for the TPS/PBS films modified by different type of oils. The addition of rapeseed oil (RO) and blackcurrant extract (BC) results in a significant improvement in the tensile strength of films compared to TPS/PBS blends without oils additives. Moreover, elongation at break parameter increases by approx. 300%. This indicates that films with amphiphilic compounds are more flexible.The optimal value of the additives are 0,5%, because for larger quantities of oil additives, the mechanical parameters are reduced in relation to the properties of the film with the addition of 0,5%.

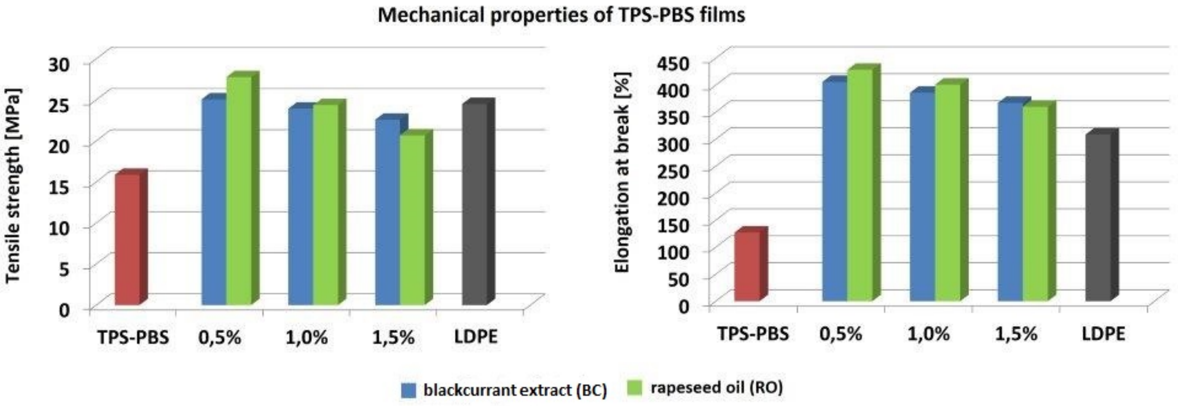

Figure 4. Tensile strength and elongation at break of TPS – PBS films.

Conclusions

Film blowing of TPS – polyester blends containing 50 wt% thermoplastic starch after optimization runs stably and smoothly on standard blown film extrusion lines. TPS – PBS films with added oils exhibited significantly improved mechanical properties. The most significant improvement of films properties was observed in the case of oil additive in an amount of 0,5 wt %. The improved mechanical properties of TPS – PBS films with oil additive showed better miscibility between the polymers.

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Efficient Synthesis of Conjugated 1,2,4-Triazole Derivatives under Suzuki Cross-Coupling Reactions in the Presence of Ionic Liquids

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Abstract* – *The new derivatives of 4-phenyl-4H-1,2,4-triazole were synthesized under palladium catalyzed Suzuki cross-coupling reaction utilizing the intermediate 3,5-bis(4-bromophenyl)-4-phenyl-4H-1,2,4-triazole and boronic acids. The transformations conducted both in the presence of conventional solvents and in ionic liquids resulted in the formation of the conjugated 1,2,4-triazole arrangements in high yields.

Keywords – Suzuki cross-coupling, heterocycles, 1,2,4-triazoles, ionic liquids, cyclocondensation.

Introduction

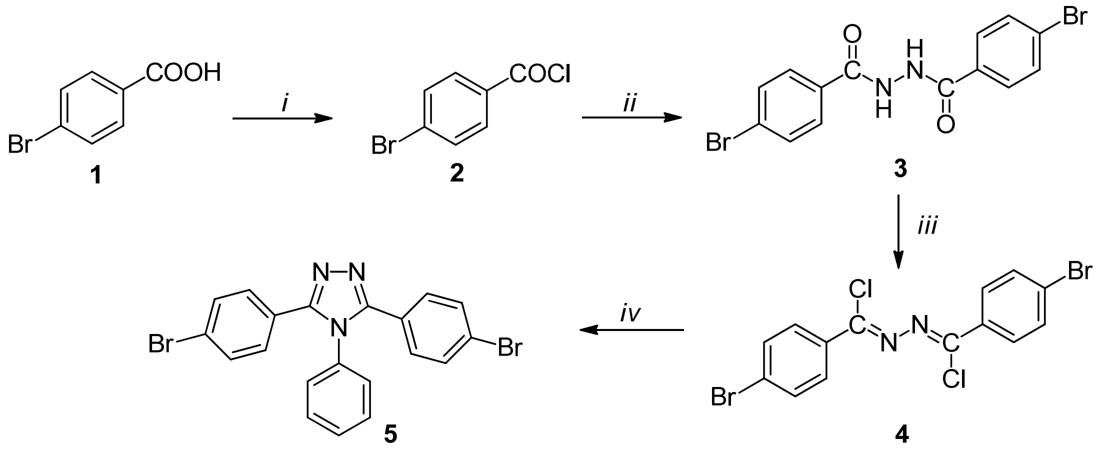
1,2,4-Triazoles belong to the group of five-membered, non-naturally occurring aromatic heterocycles [1]. The first compound from this family was prepared by Fischer in 1878 and since then the large number of precious 1,2,4-triazole derivatives were produced. They have attracted the attention of many scientists due to a broad spectrum of biological activity. 1,2,4-Triazoles display mainly antifungal (Fluconazole, Viroconazole, Ketoconazole) and anticancer (Letrozole) activities, which makes them potentially useful agents in medicine [2]. They are also applied in agriculture as potential defoliants (Amizole). Conjugated macrocyclic arrangements based on the 1,2,4-triazole core exhibit interesting electron-transfer or luminescent properties and are used in organic light-emitting diodes (OLED) or corrosion inhibitors [3, 4]. The most popular method for preparation of these heterocyclic compounds involves the reaction of diacylhydrazines with aromatic amines, in the presence of the dehydrating agent, e.g. phosphorus pentoxide, zinc chloride or N,N’-diphenylphosphenimidous amide. Other methodologies include the reaction of acid hydrazides with imidoyl chlorides, esters, nitriles or the transformations of different five-membered heterocycles, just to mention 1,3,4-oxadiazoles, 1,3,4-thiadiazoles, but also dihydro-1,2,4,5-tetrazines [5].

Over the last decades one may observe a particular interest in a new class of organic compounds called ionic liquids ILs. These modern solvents, exhibiting low vapor pressure, good thermal stability and wide liquid regions, perfectly match the principles of green chemistry in terms of process safety, environmental protection and the rational use of energy [6].

In our previous works on the application of acid hydrazides as effective reagents for synthesizing of some heterocyclic rings, we elaborated efficient few-step methodologies for the preparation of conjugated 1,3,4-oxadiazoles [7] and 1,3,4-thiadiazoles [8], making use of Suzuki cross-coupling reaction. The present study was undertaken to investigate the possibility of the preparation of another five-membered heterocyclic arrangements – 1,2,4-triazoles.

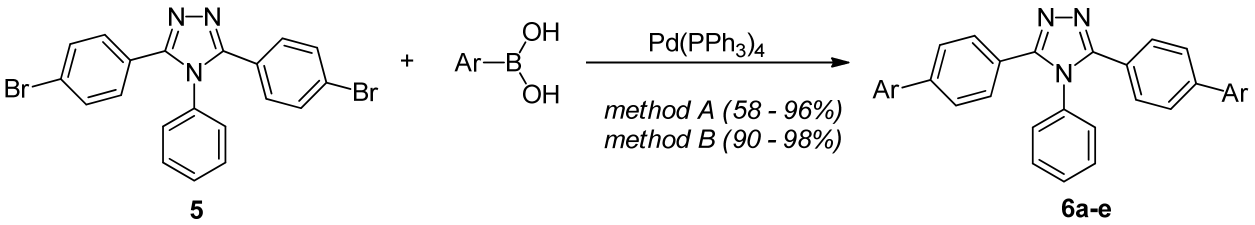
Results and Discussion

The key 3,5-bis(4-bromophenyl)-4*H*-1,2,4-triazole substituted with phenyl group at the position 4 was used as a starting material. It was prepared from commercially available 4-bromobenzoic acid (**1**), which was transferred into the corresponding acid chloride (**2**) and then substituted with hydrazine hydrate yielding the symmetrically substituted *N,N’*-bis(4-bromobenzoyl)hydrazine (**3**). The latter intermediate was transformed into the more reactive chloro-derivative (**4**) in the presence of phosphorus pentachloride and in the non-polar solvent toluene. The subsequent heating with excess aniline ($C_6H_5NH_2$) generated the key 4-phenyl-4*H*-1,2,4-triazole derivative (**5**).



Scheme 1. Synthesis of 3,5-bis(4-bromophenyl)-4-phenyl-4H-1,2,4-triazole (5) – the precursor for Suzuki cross-coupling reactions. Reagents and conditions: (i) SOCl2, toluene, reflux; (ii) NH2NH2•H2O, TEA, CHCl3, rt; (iii) PCl5, toluene, reflux; (iv) C6H5-NH2, toluene, reflux.

The next stage in the preparation of the conjugated 1,2,4-triazole derivatives was the Suzuki cross-coupling reaction - one of the most popular catalytic methods of C-C bond construction. The transformation was realized according to two methods: the conventional, making use of typical solvents (Scheme 2, *method A*) and alternative, applying ionic liquids ILs instead of common solvents (Scheme 2, *method B*).



Ar = phenyl (**a**), tiophen-3-yl (**b**), tiophen-2-yl (**c**), 4-(*N,N*-diphenylamino)phenyl (**d**), thianthren-1-yl (**e**)

Scheme 2. The conventional and alternative Suzuki cross-coupling reaction for 3,5-bis(4-bromophenyl)-4-phenyl-4H-1,2,4-triazole (5). Reagents and conditions: method A - aryl dibromide 5 (1.00 mmol), arylboronic acid a-e (2.50 mmol), Pd(PPh3)4 (0.05 mmol), NBu4Br (0.10 mmol), K2CO3 (10 mmol), toluene/H2O/EtOH (10:6:3 mL), oil bath 130 °C, 4-12 h; method B - aryl dibromide 5 (1.00 mmol), arylboronic acid a-e (2.50 mmol), Pd(PPh3)4 (0.05 mmol), choline-OH (10 mL), MW, 125 °C, 10 min.

Regardless of the method used, each reaction between the starting 4-phenyl-4*H*-1,2,4-triazole (**5**) and boronic acid (**a-e**) was conducted in the presence of 5 mol% palladium catalyst $Pd(PPh_3)_4$. The conventional transformation (*method A*) proceeded in a two-phase toluene/H_2O/EtOH solvent system and in the presence of K_2CO_3, playing a role of base, and a phase transfer catalyst NBu_4Br. The second alternative transformation (*method B*) was successfully conducted in choline hydroxide solution (IL), acting here both as a green solvent and as a base, necessary to facilitate the transmetallation step. Additionally, we found that the IL can be regenerated and recycled into the reaction with only a slight decrease in product yield after five cycles. Both presented methodologies have led to obtain a new symmetrical conjugated 1,2,4-triazole derivatives **6a-e** in high yields. However, the alternative methodology making use of ionic liquid IL has the advantage of providing the desired products rapidly, and in high yields which makes it a useful addition to the conventional synthetic protocol. The new products were characterized by elemental analysis and spectroscopic methods.

Conclusion

We have prepared a series of new 4H-1,2,4-triazole derivatives as extended π-conjugated systems. The leading 4-phenyl-4H-1,2,4-triazole ring has been coupled at the position 3 and 5 via a 1,4-phenylene linker with selected aromatic arrangements under Suzuki cross-coupling reaction. Two methodologies, the conventional, applying typical solvents and alternative, using ionic liquids, led to the final products which may be of a potential interest of optoelectronics.

Acknowledgments

Partial financial support for this research work, awarded by Polish National Science Centre grant UMO-2016/23/N/ST5/02036 is gratefully acknowledged.

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Influence Of Composition (Pd) In-, Co-Containing Aluminia- And Zirconia-Based Catalysts On Simultaneous Reduction Of Nitrogen(I, II) Oxides By CO

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It is shown that binary In-, Co-oxide supported catalysts show high activity in the reactions of simultaneous reduction of nitrogen(I, II) oxides by CO, which depends on the nature support (Al2O3, ZrO2), a sequence of the active components introduction. Structured Pd-containing In-, Co-oxide catalysts are characterized by high activity, moisture and sulfur resistance, low content of Pd (0.1) and can be used for complex purification of waste gases from nitrogen oxides and CO.

Keywords – DeNOx, In-Co-oxide catalysts, Al_2O_3, ZrO_2, CO, Pd, moisture resistance

Introduction

One of the most important challenges for scientific and applied researches is reduction of nitrogen oxides in gas emissions mobile and stationary sources, as evidenced by the introduction of morestrict norms for emissions into the environment (EURO-VI). One of the most efficient methods for neutralization of nitrogen(I, II) oxides in exhaust gases is catalytic reduction with various reducing agents (CO and CnHm). The decrease of inhibiting effect of SO_2, O_2 and H_2O to be the critical factor in the design of catalysts of elimination of nitrogen oxides from “tail” gases.

Now the main attention is focused on structured catalysts in the form of monolithic blocks, in particular, because of the wide selection of options for constructive solutions, low gas-dynamic resistance, easy placement in reactor.

Results

This paper presents the results of study of the effect of composition of In-, Co-oxide catalysts of zirconium and aluminia base as well as doped Pd (0.1%), also formed on carriers with honeycomb monoliths (Pd) In_2O_3 / Co_3O_4 / Al_2O_3 (ZrO_2) / kaolino-aerosil (KA) on their activity in the process of simultaneous reduction of N2O and NO with carbon monoxide. The influence of oxygen, water vapor and SO2 in the reaction mixture on the activity of catalysts were also studied.

It was shown that catalytic properties of composites with binary active phase differ significantly from the individual In-, Co-oxides deposited on Al_2O_3 and ZrO_2. Binary catalysts exhibit higher activity in the investigated process, which depends on the sequence of active components introduction (cobalt and indium oxides), the nature of the catalyst carrier, acidic properties of the surface. The high catalytic activity of In-Co / Al_2O_3 takes place may be the positive effect of In_2O_3 on the stabilization of cobalt in the state of Co(II) in the composition of highly dispersed cobalt oxide clusters [1]. This catalyst also characterized by greater moisture resistance: 90-98% conversion of reagents is achieved at temperatures of 450–500 °C in reaction mixtures with H_2O (fig. 1, tabl. 1).

In reaction mixtures containing excessive amounts of oxidizing agents /N_2O + NO + CO_2 + H_2O + O_2/, along with 99% conversion of NO and CO, low conversion of N_2O (17-45% at 570 ° C) can be explained with the competition of oxidant molecules N_2O, NO, and O_2 (H_2O) for the active sites of the catalyst. Clusters of cobalt(II) oxide in the Co-In / Al_2O_3 and isolated Co_2 + ions in In-, Co- HZSM-5 (FER) zeolite catalysts [2] are the active sites for NO oxidation by molecular oxygen to

NO_2 – the most reactive oxidant with respect to CO in the series: $NO_2 > O_2 > NO$. This may explain the high activity of 5% In_2O_3 / 5% Co_3O_4 / Al_2O_3 catalyst with respect to NO: at 310 ° C, 100% conversion of nitrogen monoxide and CO is achieved (tabl. 1).

The introduction of 0.1 mass % palladium into In-, Co-, Zr oxide composites significantly enhances their activity in the reduction of N_2O and NO by carbon monoxide.

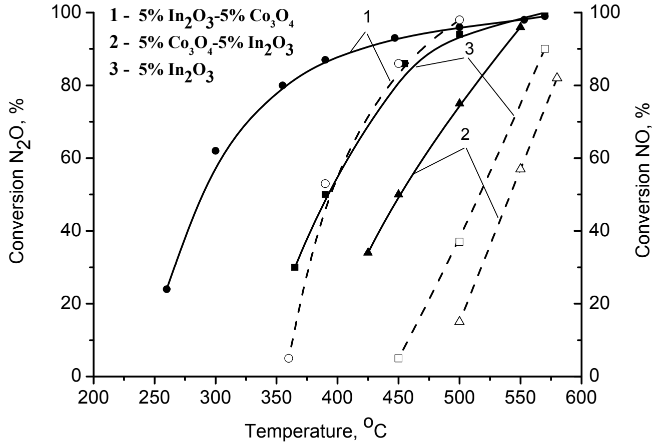

Fig.1. Temperature dependences of N_2O (solid lines) and NO (dashed lines) conversion on the catalysts In_2O_3,Co_3O_4/Al_2O_3 for reaction mixtures: 0.5% N_2O + 0.2% NO + 1.5% CO in He.

Table 1

Simultaneous reduction of nitrogen(I, II) oxides by CO in the presence of oxidizing agents (H_2O, O_2) / 0.5% N_2O + 0.2% NO +1.5% CO + 2% H_2O (5% O_2) in He; W = 6000 h^{-1}/

Catalysts (Specific surface area, m^2/g)	Conversion of N_2O[NO],%/T, °C for reaction mixtures:		
	N_2O+NO+CO	N_2O+NO+CO +H_2O	N_2O+NO+CO +H_2O+O_2
5% In_2O_3/Al_2O_3 (80)	90/480 [83/570]	93/560 [61/580]	17/570 [99/450]
5% In_2O_3/ZrO_2 (67)	55/550 [52/550]	55/550 [52/550]	-
5% In_2O_3/5% Co_3O_4/Al_2O_3 (74)	90/450 [98/500]	90/500 [91/500]	23/570 [99/310]
2.5% In_2O_3/10% Co_3O_4/ 80% ZrO_2+20% Al_2O_3 (140)	90/580 [90/570]	90/570 [90/570]	45/580 [99/380]
0.1%Pd/5%In_2O_3/7%Co_xO_y/9%ZrO_2/KA	90/450 [99/450]	90/450 [99/450]	86/500[90/500][1]

[1]/ for reaction mixtures: 0.5% N_2O + 0.2% NO+1.5% CO + 2% H_2O + 0.01% SO_2.

Conclusion

Developed granular and structured catalysts of 0.1% Pd / 2.5-5% In_2O_3 / 5% Co_3O_4 / ZrO_2 / (KA) showed high activity in the reaction of N_2O + NO + CO (90-99% conversion of N_2O and NO is achieved by temperature 450 °C), **tolerance** to the influence of moisture and sulfur compounds.

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Immobilized Catalysts In Synthesis Of Cyclic Carbonates From CO_2

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Abstract* – *The possibility of obtaining cyclic alkylene carbonates from CO_2 using immobilized catalysts in an one-pot synthesis was investigated. The synthesis proceeded in two stages: oxidation of olefin to epoxide and subsequent reaction of the obtained epoxide with CO_2. The most favorable conditions for conducting of each stage were determined.

Keywords – cyclic carbonates, carbon dioxide, immobilized catalysts

Introduction

Cyclic carbonates have a wide range of applications, among others as plasticisers and solvents, as well as in the synthesis of fine chemicals and polymers [1]. The process of obtaining cyclic alkylene carbonates from CO_2 can be carried out in two main ways: by the reaction of carbon dioxide with epoxides or alkenes [2]. Among the catalysts for these reactions the quaternary onium salts including ionic liquids deserve special attention because they are characterized by high activity.

The direct synthesis method using CO_2 and olefin as substrates is becoming more and more popular. It runs in two stages (Fig. 1). The first one involves the epoxidation reaction of terminal olefins and in the second one *in situ* formed epoxide reacts with CO_2. The advantage of this method is that both process steps can take place in one reaction vessel, so there is no need to isolate and purify the epoxide formed in the reaction. In addition relatively cheap and readily available reagents: alkenes and CO_2, are used in this process. Currently, the key challenge for this technology is the development of new catalysts with high activity and selectivity that would allow the process to run under mild conditions. A particularly interesting aspect is the search for catalysts that can be easily separated after the reaction. This will allow to simplify usually cost-intensive separation operations of the post-reaction mixture.

Results

The paper presents studies on the synthesis of cyclic alkylene carbonates from CO_2 and olefins using immobilized ionic liquids on insoluble carriers as catalysts. The tert-butyl hydroperoxide was used as an oxidant. The influence of selected reaction parameters: temperature, CO_2 pressure, amount of catalyst, molar ratio of reagents on the course of each stage of the synthesis of cyclic carbonates was determined.

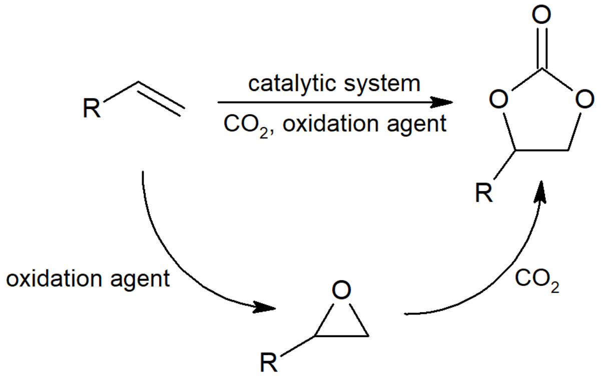

Fig.1. Scheme of synthesis of cyclic carbonates.

The effect of types of inorganic carrier such as silica, as well as the addition cocatalysts, e.g. metal halides, on the activity of catalysts in the synthesis of cyclic carbonates was investigated. It is worth noting that the process did not need a solvent addition.

Conclusion

In this paper the catalysts based on ionic liquids immobilized on insoluble supports for the direct synthesis of cyclic carbonates was investigated. The use of such catalysts allowed easy separation of the post-reaction mixture, easy catalyst separation, e.g. by filtration, and enabled repeated use of the catalyst in the next processes.

Acknowledgments

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Ionic Liquids And Supercritical Carbon Dioxide As Solvents For NHPI-Catalysed Oxidation Reactions

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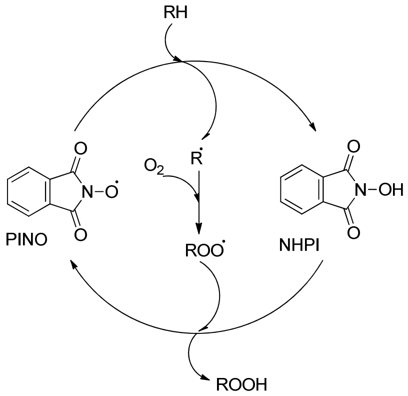
Abstract* – *Studies on the possibility of application of ionic liquids or scCO$_2$ as solvents in hydrocarbons oxidation with oxygen in the presence of N-hydrophthalimide have been reported. Various alkylaromatics (cumene, ethylbenzene, mono- and diisopropylnaphthalene, mono- and diisopropylbiphenyl) and α-methylstyrene were used as starting materials.

Keywords – oxidation, N-hydroxyphthalimide, ionic liquids, supercritical CO$_2$, cumene, α-methylstyrene

Introduction

The catalytic activity of N-hydroxyphthalimide (NHPI) in the oxidation of hydrocarbons with oxygen has been intensely studied [1-3]. The reactions proceeds via a free radical mechanism. PINO radical is formed from NHPI and abstracts the hydrogen atom from oxidized hydrocarbons (Scheme 1). PINO formation is often accelerated by addition of transition metal compounds, azo-initiators or aldehydes as co-catalysts. The catalytic activity of NHPI has been demonstrated in several processes, including cumene, ethylbenzene, toluene, cyclohexane, α-methylstyrene oxidations [1-3].



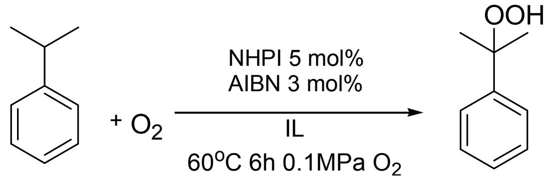
Scheme 1. Mechanism of NHPI-catalysed hydrocarbons oxidation [1-3]

NHPI has attracted considerable interest because of high activity as well as it is non-toxic and can be easily prepared from phthalic anhydride and hydroxylamine. However, due to its low solubility in hydrocarbons, most often NHPI-catalysed reactions are carried out in polar solvents such as acetic acid, acetonitrile, and benzonitrile. To eliminate or limit the amount of solvent, lipophilic derivatives of NHPI were applied [4]. Additionally, a few attempts have been undertaken to use ionic liquids (ILs) or supercritical carbon dioxide (scCO$_2$) in place of organic solvents. Advantages of ILs include low volatility, high polarity and chemical and thermal stability. Usage of CO$_2$ as a solvent is very promising because it is not toxic, its critical parameters are mild (304.2 K, 7.38 MPa), can be easily separated from a post-reaction mixture and it does not undergo subsequent oxidation reaction.

Results

NHPI-catalysed oxidation reactions in ILs

ILs composed of 1-alkyl-3-methylimidazolium cations (alkyl: ethyl [emim], butyl [bmim], hexyl [hmim], octyl [omim]) and [BF$_4$], [PF$_6$], [NTf$_2$], [CF$_3$SO$_3$], [OcOSO$_3$] and [CH$_3$OSO$_3$] as anions were used as solvents in the oxidation of cumene with oxygen using NHPI as a catalyst (scheme 2) [5].

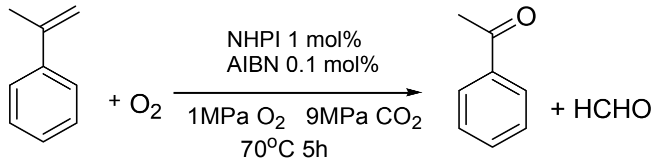


Scheme 2. NHPI-catalysed cumene oxidation in ILs [5]

High conversion of cumene (36.4%) and selectivity to hydroperoxide (100%) were obtained in [bmim][NTf$_2$]. The cumene conversion obtained in this IL was lower than those obtained in the classical polar organic solvent benzonitrile (56,7%), but higher than obtained in *tert*-butylbenzene (10.5%). [bmim][NTf$_2$] is characterized by good oxygen solubility, low viscosity as well as does not accelerate hydroperoxide decomposition. It was also demonstrated that high conversions and selectivities to appropriate hydroperoxides were obtained when [bmim][NTf$_2$] was applied as a solvent in NHPI-catalysed oxidation of other isopropyl aromatic hydrocarbons (mono- and diisopropylnaphthalene, mono- and diisopropylbiphenyl) and ethylbenzene with oxygen.

NHPI-catalysed oxidation reactions in scCO$_2$

NHPI-catalysed oxidative cleavage reaction of α–methylstyrene with oxygen in scCO$_2$ was studied [6].



Scheme 3. NHPI-catalysed oxidation of α–methylstyrene in scCO$_2$ [6]

When oxidation of α–methylstyrene was performed under pressure of oxygen (0.5 MPa) conversion of 82% and selectivity to acetophenone of 62% were achieved. When scCO$_2$ was used conversion of α–methylstyrene decreased to 52%, but acetophenone selectivity increased to 74% (scheme 3).

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Green Method For The Synthesis Of Crotonolactone And Its Thiosulfonate Derivatives

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Abstract – γ-Crotonolactone as an important intermediate synthetic product with a broad spectrum of biological effects was synthesized using the concept of green chemistry. An oxidation of furfural was carried out under mild conditions and using non-toxic reagents. The interaction of salts of aromatic thiosulfonic acids with γ-crotonolactone in an aqueous medium was studied, and new γ-[4-((phenylsulfonyl)thio)]crotonic acids were obtained. The structures of the newly synthesized compounds are confirmed by the data of IR and 1H NMR spectroscopy.

Keywords - 2(5H)-furanone (γ-crotonolactone), green chemistry, hydrogen peroxide, acetic acid, thiosulphonates, thiosulfoacid derivatives; thiosulfoesters.

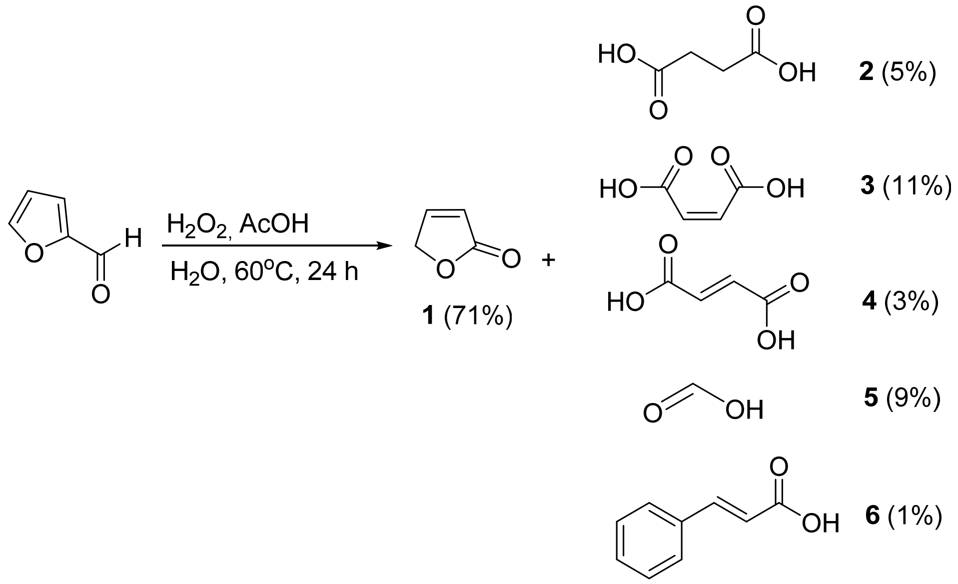
Introduction

2(5H)-Furanone (γ-crotonolactone) and its derivatives are important synthetic products with a wide range of biological effects. The use of these compounds in synthetic organic chemistry and in the national economy is well known [1]. In particular, 2(5H)-furanones are known as antimicrobial compounds. [2]. They are found in beer, kvass, contaminated food, and especially in contaminated feed exposed to mold fungi. [3]. The γ-crotonolactone derivatives attract considerable attention as plant growth regulators [4], as substances that inhibit the growth of tumors in the human body, since they are inhibitors of cell metamorphosis [5], and promoters of growth of industrial fish cultures [6].

Aromatic thiosulfoesters are structural analogues of phytoncides isolated from garlic and onions, which exhibit a wide spectrum of biological activity, and have high reactivity to nucleophilic reagents. They are effective thiolating and sulfonylating reagents, and it is also possible to use them to stabilize polymers and creatine kinase [7,8]. Thiosulfonic esters have been proposed as effective plant protection products, growth regulators [9], biocidal additives, fruit and vegetable preservatives [10], insecticides [11], radioprotective agents and medicinal substances [12,13,14]. Therefore, it is relevant to obtain new thiosulfoesters based on γ-crotonolactone.

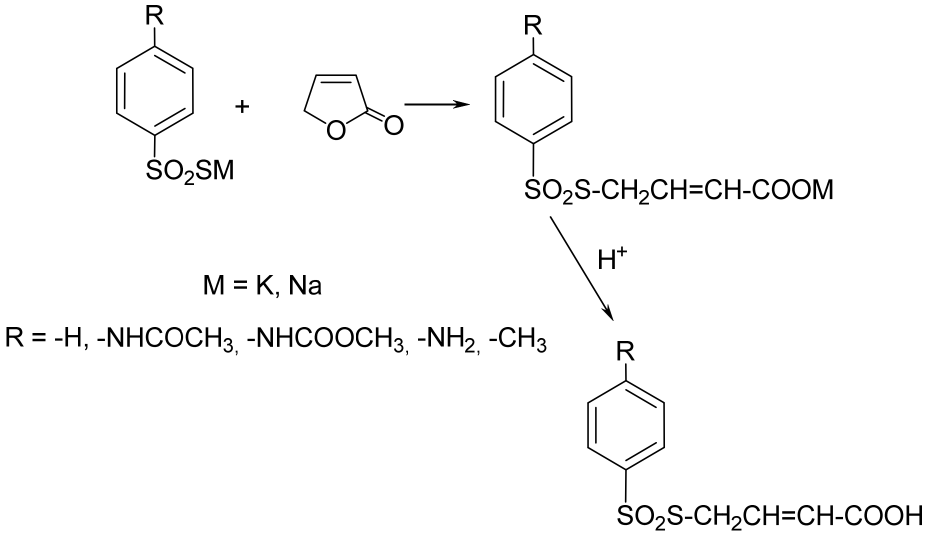
Results and discussion

We have solved the environmental problem of the method of obtaining 2(5*H*)-furanone (γ-crotonolactone), based on the concept of green chemistry. A method for the synthesis of γ-crotonolactone under mild conditions using non-toxic reagents by the oxidation of furfural with hydrogen peroxide in the presence of acetic acid in a ratio of 1: 0.05 has been developed. As a by-product in this process, a mixture of organic acids (succinic, maleic, fumaric, formic and cinnamic acids) is formed (Scheme 1). The mixture of organic acids can be used as a highly effective, environmentally friendly organic fertilizer or as a drug with a stimulating effect.



Scheme 1. Oxidation of Furan-2-carbaldehyde

γ-Crotonolactone has been used to synthesize new biologically active γ-substituted [4-((phenylsulfonyl)thio)]crotonic acids (Scheme 2).



Scheme 2. Alkylation of thiosulfonic acid salts with γ-crotonolactone

We have found that alkali metal salts of thiosulfonic acids are easily alkylated with γ-crotonolactone under conditions of the concept of green chemistry in an aqueous medium. The reaction products are salts, which, after cooling the reaction mass, were acidified with diluted hydrochloric acid, and corresponding γ-substituted [4 - ((phenylsulfonyl) thio)]crotonic acids were obtained (80-90%). t has been established that the alkylation of bifunctional salts of 4-aminobenzenothiosulfonic acid under the conditions indicated above occurs only on the thiosulfonate group. The structures of the synthesized substances were confirmed by the data of IR, ^{1}H NMR spectroscopy, the composition by the data of elemental analysis, and individuality by data of TLC.

Conclusion

A new green chemistry method for the synthesis of 2(5*H*)-furanone (γ-crotonolactone) was proposed. New promising biologically active γ-substituted [4-((phenylsulfonyl)thio)]crotonic acids under conditions of green chemistry were obtained in an aqueous medium with high yields.

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ALTERNATIVE AND NON-CONVENTIONAL ENERGY SOURCES

Biomasa One Of The Most Effective Types Of Fuel For The Production Of Warmth

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Abstract -These uses of biomass are presented in the world and prospects of her use in Ukraine as a fuel from refurbishable energy sources. The examples of equipment, developed in the institute of engineering thermophysics National Academy of Sciences of Ukraine are resulted, which uses a biofuels and the ecological use provides him.

Keywords – renewable energy sources, biomass, biofuels, thermal energy, heat output, boilers, furnaces, dryers, ecology, heat utilizers, cyclones.

Introduction

Today in the world produced over 12% of all energy from refurbishable energy sources (RES). If to look at the structure of RES, then evidently, that over 10% she is folded by energy from biomass. If all energy from RES to take for 100%, then over 72% she is folded by hard biomass. Statistical data show to us, that in the countries of EU at the production of warmth energy from biomass occupies 3 places after natural gas and coal. Thus in some countries of EU this fate considerably anymore. Yes, in Sweden part of energy from biomass in a general energy consumption anymore 20%, and in the production of warmth over 60%. In Austria of 15,5% and 39% accordingly, in Germany of 7,1% and 16,4% and for our neighbours to Lithuania of 24,4% and 16%. Why does біомаса occupy one of main places in RES? Because unit of energy from biomass in 1,6 - 3,3 times below than cost of unit of energy from natural gas. [1]

And what do we have in Ukraine with RES? The statistics show that Ukraine imports more than 60% of energy resources, and on this indicator has approximately the same indicators as Lithuania 64% and Germany 61.3%. But in these countries REE is used much better. Today, Ukraine has about 7% and plans to reach 11% of use of RES in general energy consumption by 2020, at the same time Germany plans this indicator at the level of 18%, Lithuania is even more than 40%. [2]

In Ukraine, the highest growth rate of RES is biomass. According to the Energy Strategy of Ukraine, by 2035 biomass, biofuels and waste should be in 2020 - 4%, and 2035 - 11% in the overall structure of supply of primary energy. And these are the highest rates among other RES sources. Forecast indicators show that in the production of thermal energy, the share of RES will be in 2020 - 12%, and in 2035 rubles. - 40%.[3]

This growth is planned to be achieved at the expense of increased use of RES in industry, district heating and the budget sphere. The use of biofuels in the production of energy has another feature in the development of it, there are new jobs. This indicator is the highest among other sources of energy. Thus, by 2020 more than 20,000 jobs will be created, and in 2035 the forecast will be 97,000 jobs.

And is there the necessary energy potential of biomass in Ukraine. Calculations show that the waste of the agro-industrial complex, namely straw of grain crops, rapeseed, by-products of corn production for grain and sunflower, is more than 8 million tons. In this case, their use is 30-4% of the available resources. And energy crops of about 5 million tons of AD and woody biomass (firewood, woodworking waste, drywall, etc.), biodiesel, bioethanol, peat and others. In total, this is about 21 million tons.

For the successful use of biomass it is necessary to have equipment that can work efficiently on this diverse raw material. The institute has created a solid-water heater, unified boiler KVU-0,5 t for heating and hot water supply of residential, industrial and administrative facilities in closed systems of heat supply, which works on different types of solid biofuels. The nominal heat output of the boiler is 0.5 MW, the regulation range is 40-100%, the maximum efficiency is 90%, the estimated service life is 15 years, the payback period is up to 18 months. More than 70 such boilers have been introduced.

For the heating of residential and auxiliary premises with an area of 40 to 140 m^2 and cooking, a set of furnaces of various capacity "Record" (OPV-1) was developed. OPV-1 works on different types of solid biofuels and maintains a given indoor temperature with minimal fuel consumption. Long-term combustion of fuel (not less than 6 hours at one bookmark). Nominal heat output is 2-4 kW. The additional furnace equipment allows to produce electricity 12-1-W. OPV-1 meets the requirements of State standard of Ukraine 3075-95 and Fire safety rules in Ukraine. About 500 stoves have been introduced.

The heat generator with a heat output of 0.7 MW works on different types of biofuels. It is made up of three units: a combustion and mixing unit (firebox) and two tanks with a heat output of 350 kW each. The trolleys, in connection with the peculiarities of work, include in their composition: bunkers for fine fractional fuel, a small fractional fuel storage device, a loading device for large pieces of fuel and combustion devices of a compressed layer, a heat generator introduced in the technological process of drying mineral fertilizers in a drum dryer.

The work of equipment that uses biomass should not only be energy efficient, but also meet all the necessary environmental standards. The Institute developed a heat utilizer for waste water from boilers and furnaces, which heats the water of the heat supply system by utilizing the heat of clean and dusty waste gas from boilers and industrial furnaces of various uses. Heat utilizer with a heat output of 0.3-1.2 MW intensifies heat exchange due to the use of pipes with ring turbulators, which allows to reduce the metal capacity and equipment dimensions from 1,5 2 times. The payback period is up to 1 year.

The centrifugal filter is designed to purify the airflow from ash and dust. The efficiency of dust capture in a centrifugal filter is 92-98%. The simplicity of design and reliability in operation, as well as the absence of filtering elements, makes it the most effective cyclone of the present.

Widespread use of biomass constrains a number of factors. So, the prices for natural gas for the population and heatkomunenergo are not yet marketable (40% lower). Lack of solid biofuel market. Lack of stimulation of electricity production from biomass and biogas. As a result, it is possible to conclude that today biomass is one of the most effective types of RES.

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Properties Of Gasoline With Additives Of Combustion Activators

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Abstract - The paper deals with an analysis of the problems relating to the use of special additives for gasoline. The results of experimental tests of combustion activators confirm the possibility of improving of physical and chemical characteristics and combustion efficiency of gasoline with additives of paraacetaldehyde, cumene hydroperoxide and absolute ethyl alcohol.

Key words - gasoline, additives, oxygenates, ethanol, cumene hydroperoxide, paraatsetaldehyd, absolut ethanol, octane number.

Introduction

The improvment of the internal combustion engine design put higher and higher requirements for gasoline, as motor fuel. These requirements can not be met by improving the fuel cleaning methods [1]. Nowadays, special additives, which improves fuel operational properties are added to the gasoline. They must be well dissolved in gasoline, do not cause clogging of filters and do not degrade other gasoline operational properties. All these requirements have led to the development of new special additives for gasoline to improve their properties. In the early 1950s, the problem of fuel seasonality was solved [2]. Today, the Ukrainian market offers a wide range of new brands of gasoline and additives produced by Ukrainian and foreign companies. [3]. However, modern technology of additive production has a number of disadvantages[4]. Therefore, the development of methods for improving gasoline properties using oxygen-generating additives is an important scientific and practical task.

The paper presents theoretical and practical studies of combustion activators and substances, which generate oxygen radicals in fuel. The solubility of ethyl alcohol, paraacetaldehyde and cumene hydroperoxide in gasoline has been studied. It is found that mixtures of gasoline and ethyl alcohol are unstable. Only absolute alcohol mixes with gasoline in any ratio and forms stable mixtures. Ethyl alcohol absolutization was carried out with various reagents. Although calcium oxide is an effective dehydrator, it is promising to use the tetrabutyl titanium. As a result of its hydrolysis, butyl alcohol is formed. Butanol can be used as a stabilizer of the gasoline-ethanol mixtures. [5].

The obtained results confirm the possibility of adjusting the density, combustion time and chemical stability of fuel using these additives. It was concluded that these additives, namely ethyl alcohol, are strategic for Ukraine, which has high potential for growing of raw materials for the bioethanol production.

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Nonwaste Technology of Receipt of Humic Fertilizers from Peat

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Abstract - Every country tries to be independent in everything, above all things it is for this purpose needed to have a high level of the use of own power resources. In connection with a power crisis actual is a transition from traditional energy sources to complex introduction of alternative. The complex processing of peat was probed on a fuel and extracting humic substances for the production of fertilizers.

Keywords - humic substances, peat, fertilizers, fuel, extraction.

Introduction

One of sources of alternative types of fuel there is peat which is the cheap type of fuel for a population, raw material for nourishing soils and organo-mineral fertilizers.

Humus substances - specific complexes of organic compounds of complex structure. They are divided into two main groups: a group of dark-colored humic acids, in which distinguish humic acids (gray), ulmic acids (brown) and alcohol-soluble hematomotic acids and a group of yellow-colored fulvic acids. Humic and fulvic acids taken together are called "humic substances".

An important source of humic substances is peat. Basically, peat is used for fuel and local fertilizers. If you remove humic substances from it and burn the rest, then this unique natural resource can be used more rationally. The main method of obtaining humic substances - is an alkaline reaction with solutions of ammonia or potassium hydroxide, sodium. Such treatment converts them into water-soluble salts - gumat potassium or sodium with high biological activity.

The composition of the functional groups and the structure of the molecular fragments of humic acids depends on the method of their obtaining [1].

Classical technology for the extraction of humic substances using chemical methods is based on the high temperature of the mixture, which requires high energy consumption.

We have proposed the use instead of traditional hydromechanical devices, pulsed devices of discrete pulsed energy input (DPEI) [2].

The results of the research are presented in Fig. 1.

As can be seen from Fig. 1, the lowest indices of the yield of humic substances at an extraction temperature of 20 ° C in dry peat are extracted more intensively. For comparison, a control sample obtained by conventional extraction technology at 133 ° C was investigated. The efficiency of extracting humic component from the developed technology in a pulsating apparatus of a cavitation type was investigated. The amount of sequestered humic substances is 1.4 times more than the control sample. Also, according to the developed technology, extraction from dry and milling peat occurs with the same amount of sequestered humic substances, therefore it is inappropriate to dry the peat before extraction. The extraction is carried out in a cavitation type apparatus with the same intensity for 20 minutes, 40 minutes. and 60 min Based on these studies, extraction was performed in the pulsating apparatus of DIVE for 20 minutes.

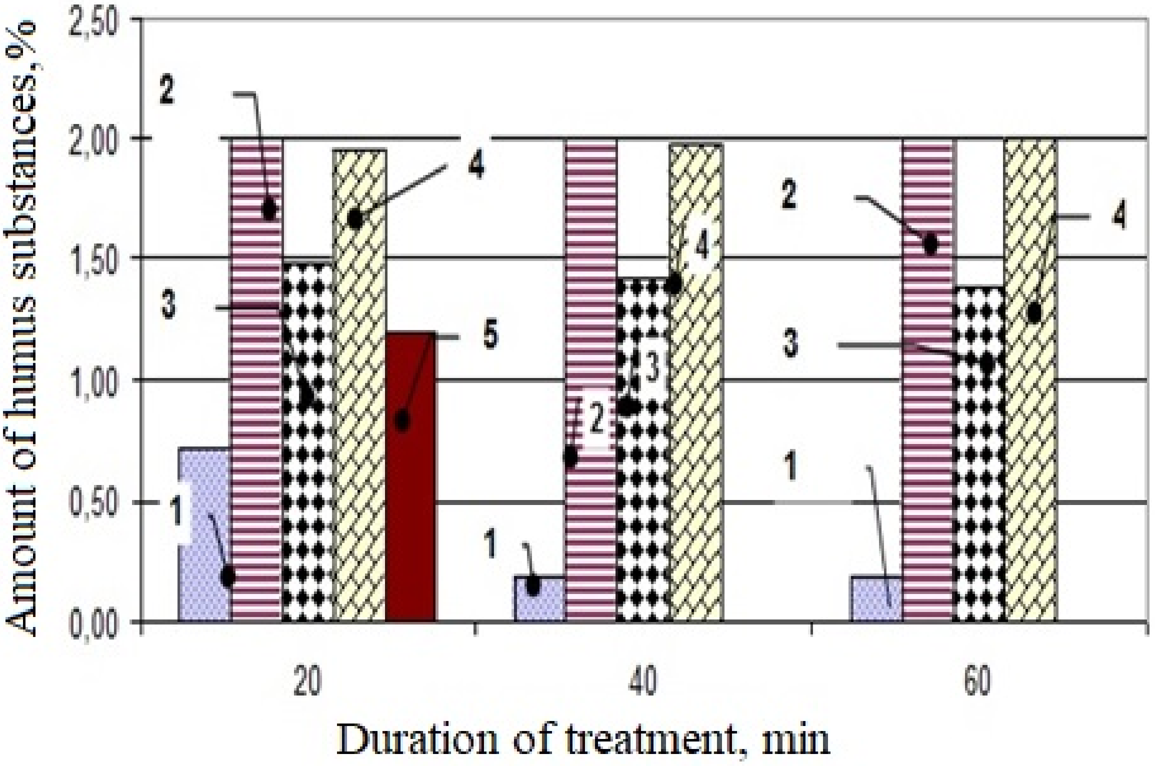

Fig. 1. Effect of mechano-thermal treatment of peat on the output of humic component:
1 - "dry" peat at a temperature of 20 ° C; 2 - "dry" peat at a temperature of 60 ° C;
3 - milling peat at temperature 20 ° C; 4 - milling peat at a temperature of 60 ° C;
5 - control sample

Conclusion

The developed technology will allow the maximum extraction of humic substances from peat with a significant decrease in temperature and extraction time, followed by the use of liquid fraction as a fertilizer, and solid residue - after extraction for the production of cheap fuel.

The use of cavitation in the technologies of obtaining humic preparations makes it possible to achieve their high physiological activity, a large yield of water-soluble organic substances, the occurrence of reactions of hydrothermal synthesis.

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Optimization Of Chemical Deposition Of HgSe Films

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***Abstract* – The process of HgSe films synthesis by a chemical deposition method, has been investigated. The optimized synthesis parameters were determined by gravimetric measurements. The phase composition, optical properties and surface morphology of HgSe films were studied.**

Keywords – mercury selenide, thin films, chemical deposition, optical properties, morphology analysis

Introduction

Mercury selenide (HgSe) is one of the least-studied of $A^{II}B^{VI}$ group thin films materials. Mercury chalcogenides can be use in IR detectors, ultrasonic transducers, catalysts, electrostatic reflective materials and solar cells due to their unique properties [1, 2]. Development of simple, low-cost and reproducible technique for the synthesis of mercury selenide films is an actual task.

Experimental

The chemical bath deposition of HgSe films was conducted with the initial working solution, consisted of mercury(II) nitrate ($Hg(NO_3)_2$), sodium thiosulfate ($Na_2S_2O_3$), as a complexing agent, sodium selenosulfate (Na_2SeSO_3), as a chalcogenizing reagent and trisodium citrate ($Na_3C_6H_5O_7$), as a pH regulator. The concentration of the $Hg(NO_3)_2$ in the working solution was 0.0025-0.015 M; $Na_2S_2O_3$ – 0.1-2.0 M; Na_2SeSO_3 – 0.0025-0.025 M; $Na_3C_6H_5O_7$ – 0.0025-0.03 M. The synthesis duration was 20-220 min, temperature – 273-313 K. The synthesis of HgSe films was carried out on preliminarily cleaned square shape glass substrates of 64.80 cm^2 in total area.

The phase composition of the HgSe films was investigated by diffractometer DRON-3.0, ($CuK\alpha^-$). Transmission optical spectra of the HgSe films were obtained on a spectrophotometer XION 500 (Dr.Lange). The investigation of the films surface morphology was performed on Atomic Force Microscope (AFM) MultiMode Nanoscope IIIa (Bruker). Elemental analysis of films was carried out on X-ray fluorescence spectrometer ElvaX Light SDD (Elvatech).

In order to optimize the synthesis process, the gravimetric measurements were carried out. The mass of deposited HgSe films were recalculated to the unit of the substrate area. For this purpose, the differences of substrates mass before and after deposition has been measured and the differences in mass were calculated. The weighing of the samples were carried out with the use of Radwag AS 220.R2 analytical weight (accuracy – 0.0002 g) depending on the concentrations of initial reagents in the working solution, the synthesis duration and temperature.

Results and discussion

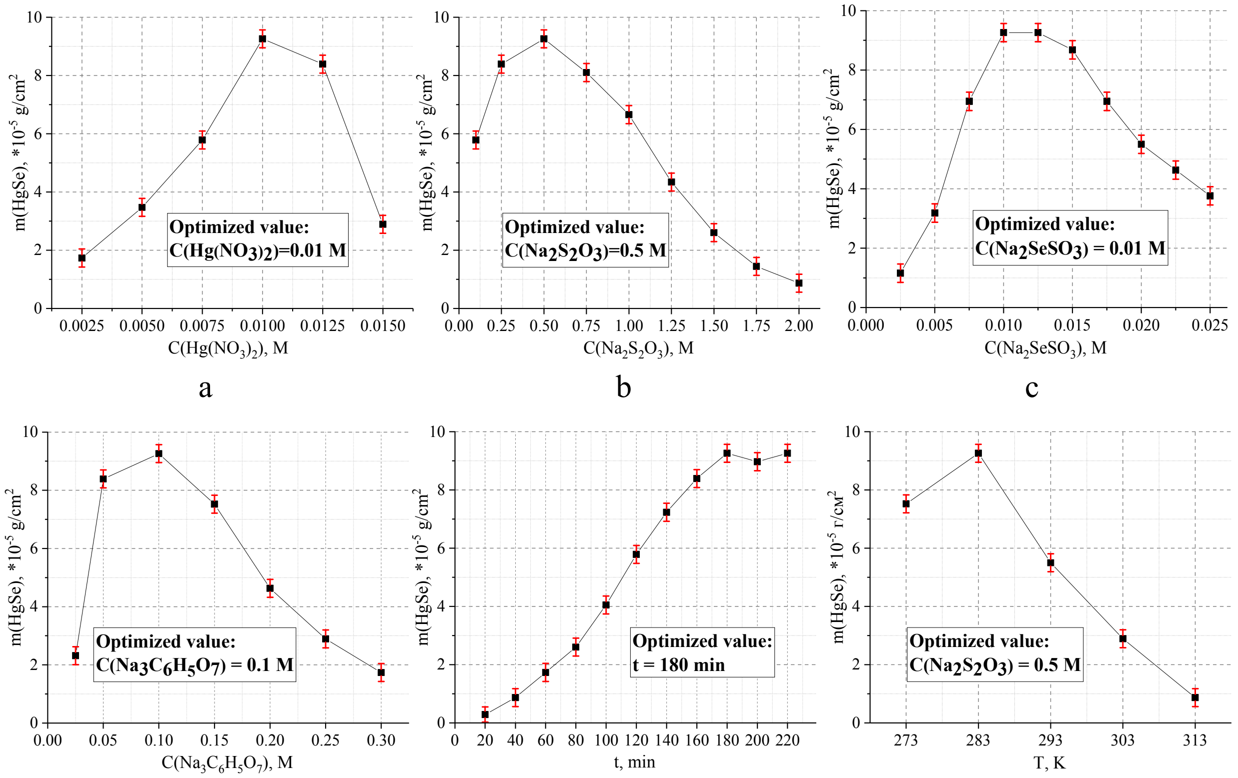
The X-ray analysis of HgSe films has been held. Peaks that corresponded to the cubic phase of zincblende (sphalerite) structure were identified on diffractogram.

The optical transmission T(λ) of HgSe films were investigated for wavelengths from 340 to 900 nm. The increasing of the light transmission are present at ~ 450 nm region. The spectral dependences in $(\alpha \cdot h\nu)^2$ vs. $h\nu$ coordinates allow to determine the values of fundamental absorption edge. The optical band gaps of the HgSe films are localized in the ranges 1.38-2.50 eV.

AFM studies of the surface morphology of HgSe films, showed that coating is solid and homogeneous. The coatings surface are packed of irregular shape particles. Their size innceases with increasing of deposition duration.

The microanalysis of the HgSe films surface shows nearly stoichiometric atomic ratios of mercury to selenium with a slight excess of Se atoms.

By gravimetric measurements of deposited HgSe films, the dependences of mass changes on the synthesis conditions were constructed. The research results are presented in Fig. 1. The optimized synthesis parameters were found by greatest HgSe film mass on the each dependence.



a b c

d e f

Fig.1. Dependences of films mass changes of HgSe per unit of substrate area on the concentration of: a – Hg-containing salt, b – $Na_2S_2O_3$, c – Na_2SeSO_3, d – $Na_3C_6H_5O_7$, e – synthesis duration, f – temperature of synthesis.

Conclusion

The HgSe films were synthesized by chemical deposition method. The optimal synthesis parameters are found. They are follows: concentration of mercury salt, trisodium citrate, sodium thiosulfate and sodium selenosulfate in the working solution – 0.01 M, 0.1 M, 0.5 M, 0.01 M, respectively, 283 K of temperature and 180 min of synthesis duration. The phase composition, optical properties and surface morphology of HgSe films were studied.

Acknowledgments

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Thermal Decomposition Of Thermally Treated Granulated Wood

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***Abstract* – The derivatographic method was used to study the thermal decomposition of pine wood, which was thermally treated in the form of granules at atmospheric pressure under its own gas environment. It is shown that an increase in the treatment temperature from 250 to 300 °C leads to the temperature range extension of decomposition of the fuel and an increase in its calorific value.**

Keywords – derivatography, wood, torrefaction, thermal treatment, thermal decomposition, temperature and heat of thermal decomposition

Introduction

Plant biomass is an important source of renewable raw materials and energy. However, low energy density, instability of granulometric composition and physical properties, and also biological activity and dispersion over the territory are the main problems in its energy and technological use [1]. It is necessary to improve fuel properties of biomass for more efficient its using as an energy source. One of the ways of such an improvement is granulation, which allows to increase the specific heat of combustion, and also to improve transportable characteristics. A promising step is torrefaction of biomass in increasing the energy density and efficiency of biofuels using. Torrefaction is a mild pyrolysis process in an inert atmosphere, in the temperature range of 200–300 °C. The thermal destruction observed in this process is accompanied by a change in the mass and composition of the biomass. As a result, the percentage of oxygen decreases and the content of hydrogen and carbon increases, which leads to an increase in heat of combustion [2]. Torrefaction allows to maximally approximate the properties of biofuels to the properties of energy coals. The yield and calorific value of the finished product depends on the depth of thermal treatment. Therefore, when studying the torrefaction process, developers try to find the optimal mode that allows one to achieve the highest calorific value with the least loss of the initial energy. Various types of biomass can be subjected to torrefaction, including agricultural waste and "energy crops" that have fairly similar physical and chemical properties [3].

Materials and methods

Granules of pine wood with a diameter of 8 mm and a length of 30–40 mm was charged into the steel non-hermetic containers and subjected to thermal treatment in a muffle furnace in their own gas medium at atmospheric pressure. The temperature of the material during thermal treatment process was measured with a thermocouple passing through a hole in the lid of the container. Upon reaching the muffle furnace temperatures of 250, 260, 270 and 290 °C, a container with granules was placed in the furnace. The warm-up time of the material to the set temperature was 30 minutes. After warming-up thermal treatment process was continued for 60 minutes. The destruction of wood is an exothermic process and therefore the temperature of the material has increased. By the end of thermal treatment, the material temperature exceeded the base temperatures of the muffle furnace by 15 K at 250, 260 and 270 °C and by 10 K at 290 °C. At the expiration of thermal treatment time, the containers were removed from the muffle furnace and cooled to room temperature.

The obtained fuel samples were subjected to thermal analysis in the range of 20–1000 °C with a temperature scanning rate of 7.4 K/min on the derivatograph Q-1000, modernized at the

IET of NAS of Ukraine. Before the study, the fuel samples were ground in a porcelain mortar and placed in a conical ceramic crucible from the instrument kit. In the crucible of comparison was an inert substance – Al_2O_3. The temperature scale was corrected using the transition temperature of quartz from α- to β-form (573 °C). The temperature deviation did not exceed ±0.5 K. The collection and processing of information from the channels of measurement was performed using the applied computer program "Derivatograph".

Results

A derivatogram of a sample of fuel obtained after thermal treatment of wood granules at 270 °C is shown in Fig. 1 as an example. To compare the results of thermal treatment, the wood of the initial granules was subjected to thermal analysis. As can be seen from the curves of change in mass velocity (DTG) and differential thermal analysis (DTA), bound water is removed in the initial heating period (up to 150–190 °C).

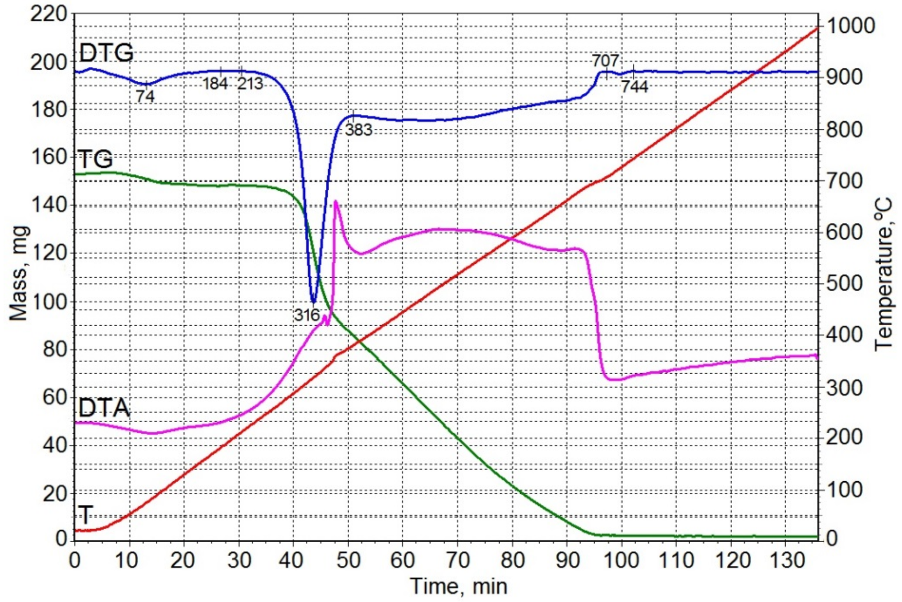

Fig.1. Derivatogram of fuel obtained after thermal treatment of pine wood granules at 270 ºC.

The components of wood decompose in different temperature ranges, which cause the multistage nature of its destruction. Thermal decomposition of hemicelluloses occurs in the temperature range of 225–325 °C, cellulose decomposes in the range of 305–375 °C, and lignin is characterized by a gradual decomposition from 250 to 500 °C [1].

An analysis of the DTG curves showed that the proportion of the mass of the sample of untreated wood, which thermally decomposing in the temperature range from complete dehydration to 325 °C, is 36.8 %. When the temperature of thermal treatment is increased, this proportion decreases from 27–28 % at 250–260 °C to 11.4% at 290 °C. This indicates a decrease in the content of hemicellulose in the composition of the resulting fuel.

Thermal treatment of wood expands the temperature range of thermal destruction, which follows from the DTA curves shown in Fig. 2. For wood treated at 250 °C, thermal decomposition is observed in the range from 203 to 727 °C. While for untreated wood, destruction starts at 170 °C and ends at 606 °C. An increase in thermal treatment temperature leads to a shift in the temperature of the end of thermal decomposition to higher temperatures (up to 788 °C for the treated at 290 °C).

Evaluation of the heat of thermal decomposition showed that the mild thermal treatment of pine wood leads to an increase in the specific heat of thermal decomposition. The increment of specific heat in comparison with the specific heat of untreated wood increases with increasing thermal treatment temperature by 18–20 % at 250–260 °C and 27 and 39 % at 270 and 290 °C, respectively.

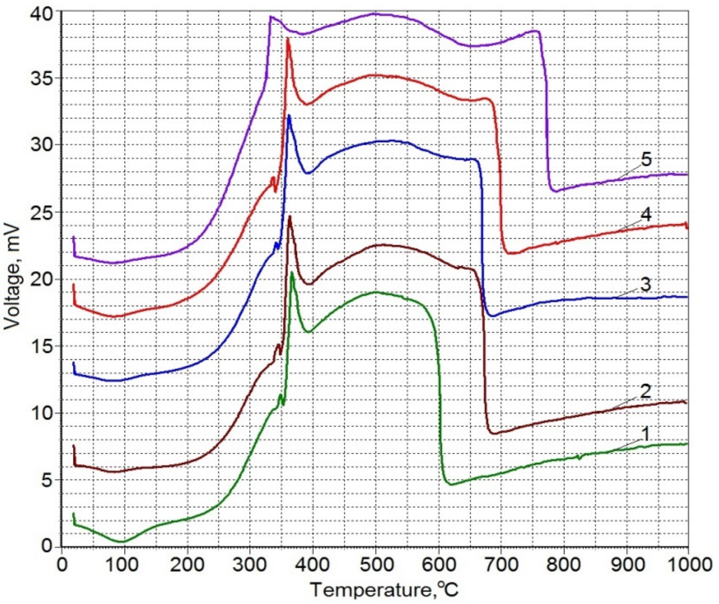

Fig.2. DTA curves of pine wood granules before (1) and after thermal treatment at 250 (2), 260 (3), 270 (4) and 290 °C (5).

Thus, the calorific value of pine wood can be increased from 15.5 to 21.5 MJ/kg due to thermal treatment. The ash content of thermally treated wood is slightly higher than the initial (before treatment – 0.76 %, after treatment at 290 °C – 1.84 %). Thermal effect on wood causes a reduction in the number of hydrophilic active centers, which leads to an increase in the hydrophobicity of the fuel, and, consequently, to a decrease in its equilibrium moisture. The moisture of the granules after thermal treatment and storage was in the range of 2.65–3.74 %, while the moisture of the untreated granules stored under the same conditions was 7.33 %.

Conclusion

Thermal analysis of torefied pine wood granules showed that the degree of its decomposition depends on the temperature and time of thermal treatment. Torrefaction is an effective way to improve the energy characteristics of biofuels.

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Operating Modes of the Advanced Purification Technology for Graphite Application in Lithium-Ion Batteries

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***Abstract* – The subject of the study is the influence of the ash content in Ukrainian natural graphite on treatment duration in thermal refining natural graphite to battery grade. At temperatures 2900-3000℃, the required purity can be achieved in 5-15 minutes regardless initial level of impurities.**

Keywords – lithium-ion batteries, natural graphite, thermal purification, operating modes.

Introduction

Within the next five years, it is expected a huge expansion of the batteries graphite global market due to the growing demand for electric vehicles and electric storage stations. The major challenge related to this development is there are a few scalable technologies, in particular thermal [1] and chemical [2] treatment, applicable in industry that can potentially meet all market requirements such as product output and purity. However, it is supposed only the thermal process has respective capability to produce so-called "green" purified graphite of 99,95-99,98% carbon grade in environmentally friendly way with low carbon dioxide footprint. That can be achieved by wide application of renewables at different stages of the technology as well as heat waste recovery from final product.

In this connection, for more than ten years, National Metallurgical Academy (NMAU) along with Thermal and Material Engineering Center (TMEC) has been working on the advanced thermal purification technology based on electro-thermal fluidized bed (ETFBP) with specific focus on product quality, energy consumption rate and environmental impact to surpass existing analogues.

Objectives of Study

The duration of graphite treatment via ETFBP defines the furnace productivity and depends on different factors like initial amount of impurities in precursor material, particle size, operating temperature and required product purity. Therefore, the main objective of the current study is to figure out whether there are perceptible time limits for purification of natural graphite with various initial ash content in range 0,4-27% at temperatures 2900-3000°C.

Research Method

For this purpose, a laboratory furnace of 5 kW power was developed, Fig. 1. The furnace consists of a crucible, resistive heater, thermal insulation, inert gas and electric supply systems. The size of the operating space ensures up to 50g payload of carbon material for treatment at temperatures 1000-3000°C.

In small reactors like this one with harsh inner environment, the issue of temperature measurement methods is crucial. Thermo-couple sensors do not fit for this purpose and can be installed only in isulation. Thus, they would not transmit accurate data on real state of a sample. On the other hand, heat losses do not allow to apply pyrometers, because that affects inside temperatures. Therefore, our team decided to control the regime in accordance to an operating curve which ties the temperature value with the electric current passing through the resistive heater.

The operating curve was built on the basis of preliminary study of the behaviour of various control-samples (‘witnesses’) during heating them and soaking at set electric parameters. The samples were made of copper, stainless steel, corundum ceramic and some carbides – materials with known melting point. According to our evaluations this solution secured measurement accuracy in range ± 75°C that is comparable to pyrometers performance.

Fig.1. The laboratory reactor for thermal purification.

As a gaseous inert agent, Argon was used. Before every purification cycle the furnace was blown with a small Argon flow, approximately 1 L/min, for 5 minutes and sequentially heated up at 0,8-1,2 kW power for 10 minutes, that was enough for replacement of air and water evaporation from the inner parts. Further, according to the operating curve, the electric power was being increased up to 3,6-4,5 kW to maintain set temperatures level for time period from 5 to 20 minutes.

Purified samples was being weighed and tested on physical and chemical properties. To evaluate graphite quality, there were also used the microscope Tescan Mira 3 LMU, detector Oxford X-max 80, conventional ‘lost on ignition’ test and laboratory method for measurement of graphite electric resistivity.

Results and Discussion

The considerable achievement of the completed work is the furnace, which has been designed and developed by our team, has demonstrated outstanding performance with sufficient withstanding of high temperatures and impact of various chemical impurities on the crucible, thermal insulation and resistive heater. The duration of purification cycle including blowing, heating, soaking and cooling has been decreased to 30-40 minutes that provide us the possibility to conduct multiple experiments, up to 8-10, during one shift.

According to the experimental data, at temperatures 2000-3000ºC, impurities volatilization occurs with high rate of reaction. That has been also proven by visual observation – the ‘cold’ furnace elements made of quartz glass were changing their transparency promptly within 30-60 seconds.

The typical results are presented in Table 1. The sufficient graphite purity of 99,99% has been secured at temperature level > 2900ºC equally for all samples of initial ash content 0,4-27%. The time limitations of the purification process are mainly related to the heating-up rate of the inner layers of samples. In samples of small weight from 5 to 10 g, the graphite can be purified within 5 minutes. There was a regularity in the study that should be also mentioned. The traces of Ca, Fe and Ti are present in the product relatively at considerable amount.

Therefore, the study has proved capabilities of high thermal purification of natural graphite in 5-15 minutes. The results will be used for justification of operating modes of ETFBP technology for Ukrainian raw materials. The developed experimental approach is to be used for other carbon materials like biochar, metallurgical and petroleum coke, carbon black, brown and hard coal, anthracite with focus of their further application in various industrial processes.

Table 1

Impurities content after thermal purification of natural graphite from the Ukrainian mine

Type of impurities	Precursor material	Purified material	Units
Total Ash	10.58	< 0.01	%
Al	7337.2	-	ppm
Si	18134.1	< 2.8	ppm
S	1082.3	-	ppm
K	2072.6	-	ppm
Ca	1917.1	< 11.1	ppm
Ti	453.9	< 15.5	ppm
V	94.2	< 2.2	ppm
Mn	280.4	-	ppm
Fe	29377.5	< 27.5	ppm
Cu	351.3	-	ppm
Zn	561.8	< 1.2	ppm
Mo	84.6	< 4.3	ppm

Conclusion

The laboratory furnace of 5kW power for graphite purification is developed and tested.

The subject of the study is the influence of the ash content in Ukrainian natural graphite on treatment duration in thermal refining the material to battery grade. At temperatures 2900-3000°C, the graphite grade of 99,99% can be achieved in 5-15 minutes regardless initial level of impurities. The results prove efficiency of the ETFBP technology and can be used for its adjustment for Ukrainian graphite,

Acknowledgments

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Catalytic influence of native minerals on thermochemical conversion of salty coals

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Abstract* – *The possibility of involvement of salty coal (SC) into the fuel base of Ukraine is considered. SC has high fuel indexes, but has an abnormal level of alkali metals in its composition. The changes of ash content and elemental composition of coal after water extraction are shown. The influence of alkali and alkaline earth metals salts on thermochemical conversion of salty coal at different temperatures and particle size of coal is determined.

Key words – salty coal, mineral matter, thermolysis, catalytic action, gaseous products, burning rate

Introduction

Coal with high content of alkali and alkaline earth metals (salty coal) occupies its definite place in an energy reserve, not only in Ukraine but also in many other countries, including China, USA, Russia, Germany and Australia. The deposits of salty coals in Ukraine are located in the Western and Northern Donbas, total explored reserves of ~ 12-25 billion tons.

Compounds of alkaline metals (alkali, salts) are universal catalysts (reagents) in many processes of thermal conversion of fossil fuels and biomass [1]. This applies to artificially introduced reagents and natural minerals, which are component parts of fossil fuels.

Salty coal (SC) stands out among other fuels not only by problems at traditional combustion (slagging, corrosion), but also that it contains a natural catalytic complex - alkali and alkaline earth metals salts, iron sulfides [2] and some of catalytically active trace elements in significant amounts. In our works [3] it is established that in salty coal of different deposits of Ukraine there are not only sodium chloride, but also sodium and calcium sulfates in significant amounts, which were clearly identified from aqueous extracts.

The purpose of this work was to determine the role of natural water soluble compounds in the processes of thermolysis of the salty coal of Bogdanovsk deposit (Northern Donbas) (table 1). It has a different content of sodium chloride (compared to Novomoskovsk SC) and another composition of water-soluble minerals, but not more attractive energy characteristics.

Table 1.

Characteristics of salty coal of Bogdanovsk and Novomoskovsk deposits

Deposit	Heat of combustion Q^{daf}, kcal/kg	Ash A^d, %	Volatiles V^{daf}, %	Na_2O in ash, %	Chloride Cl, %	Sulfur S, %
Novomoskovsk	7200-7500	10,1-15,0	44,0-47,3	0,6-1,0	0,6-0,9	2,1
Bogdanovsk	7020-7580	12,6-14,6	41,2-42,6	0,5-0,7	0,3-0,6	1,6-2,1

Experimental

Experiments were carried out at the Coal Energy Technologies Institute of the National Academy of Sciences of Ukraine at the facility of «Pyrolysis M». This equipment is designed to study the dynamics of gas evolution and combustion of the coke during thermal contact pyrolysis of coal in a fluidized bed at atmospheric pressure.

Samples of salted and desalted coal are crushed and dispersed to three fractions of particle size of 0.2-0.63, 0.63-1 and 1-1.6 mm. Extraction of salts from coal was carried out according to the parameters optimized in previous studies [4]: time (5-10 minutes), temperature (20 oC) and the ratio of solid phase to liquid (T:P=1:3). It should be noted that desalting resulted in some changes in the elemental composition (dry mass) of samples of salty coal (fig.1). As a result of desalting there was a decrease in the concentration of oxygen (a decrease in content by about 2-3%), a less significant reduction of hydrogen (about 1%) and nitrogen (by ~ 0.5%). Loss of sulfur content did not exceed 0.25%, and ash content was reduced by 0.5-2%. At the same time, carbon content increased substantially from 74 to 80%. Losses of oxygen, nitrogen and hydrogen can be explained by extraction during water desalting, so-called fulvic acids - water-soluble organo-mineral compounds. The reduction of the total sulfur content may be due to the presence of sulfates in the water-soluble salts of minerals and their removal by aqueous extraction.

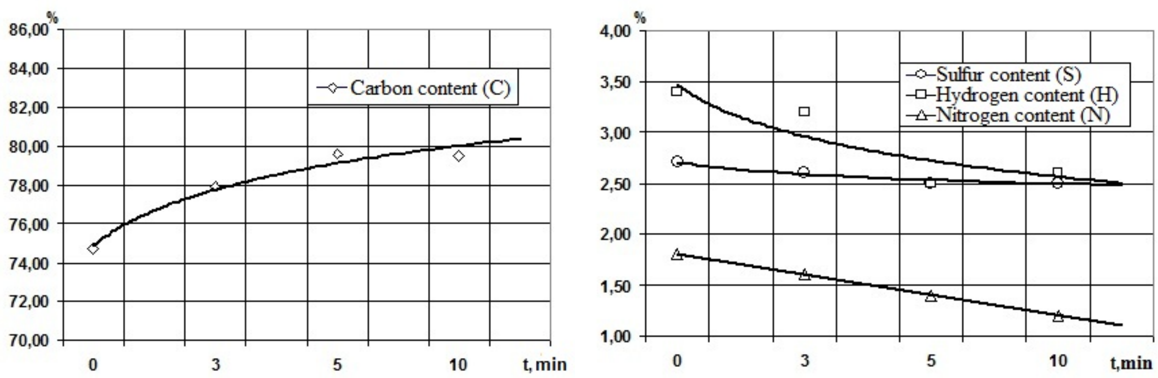

Fig.1. The content of macroelements in organic mass of coal depending on the time of desalination

The study of thermolysis was carried out at the temperatures of the fluidized layer of inert material (sand) at 550, 650, 750 and 850 ° C. As a result of the study, it was determined that the yield of gases (H2, CO, CO2) during combustion of salty coal is much more intense than that of combustion of desalted coal, as at the characteristic time (5 vs. 10-15 seconds) of the first stage of pyrolysis, and at the maximum yield of H2, CO, CO2 (Fig. 2). This is true for all particle size fractions studied.

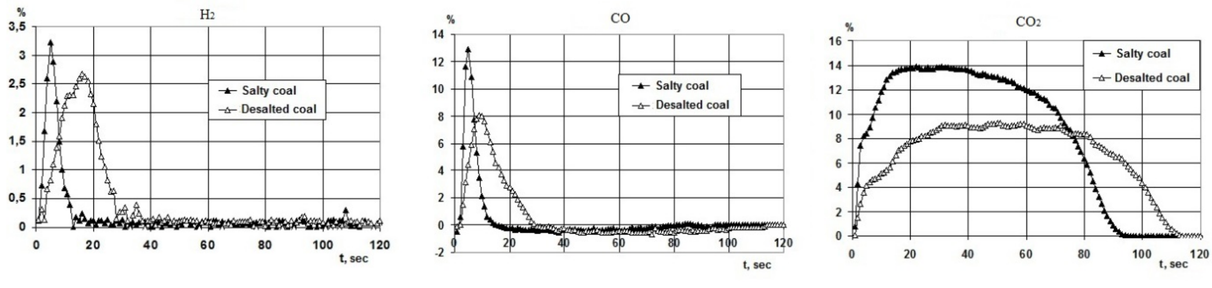

Fig. 2. The yield of gaseous products H_2, CO, CO_2 depending on the time of thermolysis (coal weight 0.5 g, temperature 750 ^oC, particle size 0,63-1 mm)

Particularly clearly, the difference can be seen at lower temperatures where the emission zones of volatile and combustion of coke are identified. It can be to claime that water-soluble minerals of salty coal (sodium chloride, sodium and calcium sulfates) give the process of formation and conversion (combustion) of volatile substances a significant catalytic effect. The same effect was observed in manuscript [5]. Native water soluble minerals have strong influence on decarboxylation reactions too (Fig.2).

On the other hand, as we see from Fig. 3, in the range of burning temperature 550-850 ^{o}C, the combustion rate (lnW) of coke residue (after devolatization) of salty coals (the main reaction $C + O_2 = CO_2$) is insignificantly different from the samples that ones were desalted by water washing.

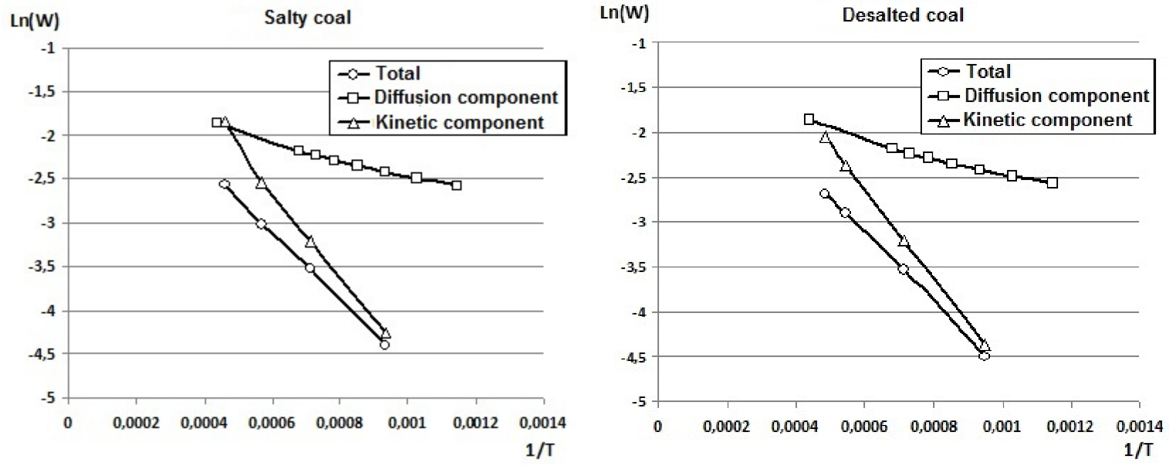

Fig. 3. Dependence of the carbon burning rate on the process temperature

Conclusions

1. The catalytic action of native salts is more pronounced in the stage of gas formation and is less significant at increasing the temperature of thermolysis.
2. The ratio of H_2/CO for initial salty coal at the maximal yield consist of from 0.36 to 0.40, while for desalinated coal it is 0.25 - 0.34. This indicates a more significant influence of alkaline salts on dehydration reaction than on the process of decarbonilation.
3. Native water soluble minerals have strong influence on decarboxylation reactions.
4. The presence of a natural catalytic complex in the composition of salty coal gives a certain perspective for the use of salty coal in a blends with other coal, which does not contain an catalytic alkaline additions and is characterized by more refractory ash.

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Current Status Of Municipal Solid Waste Management In Ukraine

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Abstract –The status of existing legislation on waste management in EU, Ukraine and worldwide has been considered. Special features of EU Directives on waste management are considered. Different technologies of waste utilization including grate firing, gasification and pyrolysis and plants performance where they are used are briefly analyzed. Special attention is drawn to current situation in Ukraine related to MSW.

Keywords – waste management, municipal solid waste (msw), refuse derived fuel (rdf), incineration, best available techniques, waste-to-energy plant.

Introduction

On 16 September 2014 Verhovna Rada (Supreme Council of Ukraine) and European Parliament simultaneously approved Association Agreement between the European Union and the European Atomic Energy Community and their member states, of the one part, and Ukraine, of the other part. This EU-Ukraine Association Agreement completely entered into force on 1 September 2017 becoming a part of national legislation. As a result it is assumed stepwise approaching the Ukrainian legislation to EU one in the field of energy efficiency, renewable energy sources, climate change, tax on emissions and wastes as well as waste management. According to Association Agreement the obligations of Ukraine related to climate change are defined. In the Agreement the protection of the environment is considered to be high priority one as well as harmonization of national legislation with policy and laws of EU in the field of the environment protection in 8 sectors: 1) environmental governance and integration of environment into other policy areas; 2) air quality; 3) waste and resource management; 4) water quality and water resource management, including marine environment; 5) nature protection; 6) industrial pollution and industrial hazards; 7) climate change and protection of the ozone layer; 8) genetically modified organisms.

Policy regarding the waste management in EU is defined by eight Directives from which three ones are included in the list of Agreement: 1) Framework Directive 2008/98/EC of the European Parliament and of the Council of 19 November 2008 On waste and repealing certain Directives; 2) Council Directive 1999/31/EC of 26 April 1999 On the landfill of waste; 3) Directive 2006/21/EC of the European Parliament and of the Council of 15 March 2006 On the management of waste from extractive industries. The implementation of the above Directives needs significant changes and additions to national legislation relevant to waste management. The time period of introduction of Directives is to be from 2 to 5 years from 2019 till 2022.

Framework Directive 2008/98/EC regarding waste sets legislative base and main rules on waste management which allow both to decrease the amount of waste storage and to provide resource saving due to re-use and treatment of secondary feedstock. Directive sets implementation of hierarchy of priorities on waste regulating including: prevention and minimization of its formation (due to economic stimulation – incentive, special tax, educational campaign etc); preparation for re-use; treatment, including composting; utilization incl. energy re-use; ecologically safe storage at disposal dump. To achieve high quality of waste treatment, Directive obliges to introduce separate gathering of waste at least paper, metal, plastics and glass. Waste utilization is the use of waste as secondary material or energy resources. Definition of "re-use" also covers production of alternative fuel from waste including MSW. Directive sets up unified waste classification in EU member states including hazardous, regulating the order of how to classify wastes as hazardous and control them. Such classification is set up by the Decision of Commission 2000/532/EC of 3 April 2000. Directive obliges introduction of principle «contaminators pay» by means of extended responsibility for producer – financial and organizational mechanism of provision to closed loop of treatment. This means that producer takes responsibility for treatment and utilization of its goods after consumption. Directive also obliges to follow obligations related approval certain procedures related to producer. Necessary condition needed to obtain approve on combustion or co-firing of wastes aimed at energy utilization is the necessity to re-use energy as energy efficient as possible.

Basic EU document in the field of protection the environment that regulates emissions from industrial plants is Directive 2010/75/EC of 24 November 2010 p. - (the Industrial Emissions Directive or IED). Directive IED aims to achieve high degree of protection of the environment by means of decrease in harmful industrial emissions by implementation of Best Available Techniques or BAT. Term "best" means most effective from the standpoint of achievement of high general level of environment protection. Directive has criteria to define BAT (Annex III). Directive IED also covers waste management – waste combustion, storage at landfill. According to Directive 2010/75/EU, operation of waste incineration (and co-incineration) plant can be done only in case of availability of integrated permit. The conditions of the permit are formulated on the basis of Reference Document On The Best Available Techniques (BREFs) For Waste Incineration (WI BREF) 2006. In 2019 it is planned to announce new WI BREF.

On 28 March 2019 President P. Poroshenko signed Law «On Basic concept (strategy) of ecological policy of Ukraine by the period of 2030 year». This law makes provision the decrease in the amount of waste storage at landfill dumps in 2030 till 35%. Important phase of implementation of conditions of EU directives relevant waste management is adoption of National strategy on waste management in Ukraine till the year of 2030 (Regulation of SCU of Ukraine № 820-p of 8 November 2017). The strategy will formulate general directions and define state policy in the field of waste management. The objective of the Strategy is to clean the environment and decrease waste that goes to landfill. Priority direction is to convert waste on resources and decrease amount of waste. Strategy covers all territory of Ukraine and considers such waste source as MSW, construction waste, hazardous waste, another industrial waste (except for hazardous), agricultural waste, electrical and electronic waste, charged-out batteries and accumulators. Tools to realize the Strategy is National plan to manage wastes approved by SCU of 20 February 2019. National plan defines tasks and applied measures which implementing allows for Ukraine to implement a new model to manage waste as that being in force in EU. National plan to manage waste, in particular, foresees formulation of public policy in the field of waste management, creation of effective system of waste gathering and its disposal etc. Framework draft-law "On waste management" is at the final stage of approval. Beginning from 01.01.2018 the correction to Law of Ukraine «On waste» (art. 32), was put into force forbidding storage of un-treated MSW at landfills.

Main material

MSW is classified as waste that is gathered by municipality or another municipal authorities. In most cases MSW includes: household waste, waste formed in gardens, yards, parks, waste from retailers and public organizations.

The amount of MSW in Ukraine during the last years is considered to be 10–12 mln t (50–60 mln m3) (Table. 1, source: Ministry of regional development, construction and municipal industry of Ukraine, Public Bureau of statistics of Ukraine). In 2000 in Ukraine it was produced about 180 kg of MSW per person, but in 2017–2018 it exceeds 250 kg. Only 77–78% of population in Ukraine can obtain service on MSW disposal. Beside this, in 2017 p. it was formed 11,8 ths t of MSW of 1–3 hazardous class and only 1.9 ths of them was disposed in special landfills.

Table 1

MSW management in Ukraine in 2014–2018

Year	Amount of gathering		Points of secondary feedstock	Waste management plants	Site for compo-sting	Incineration plants		Landfills	
	ths t	kg/person	ths t	ths t	ths t	ths t	%	ths t	%
2014	10748.0	250.0	142.3	73.0	0	149.5	1.4	10383.2	96.6
2015	11491.8	268.5	132.5	128.3	2.8	254.3	2.2	10973.9	96.6
2016	11562.6	271.0	126.6	143.8	1.6	256.7	2.2	11033.9	95.4
2017	11271.2	265.3	146.2	259.9	0.97	246.7	2.2	10615.1	94.2
2018	10679.3	253.7	146.5	260.1	1.6	208.1	1.9	10063.0	94.2

In 2018 in Ukraine it was treated and utilized just 5.8% of MSW, incl. 1.9% was incinerated (burnt-out), 3.9% went to gathering sites, points of secondary feedstock and incineration plants. 26 MSW sorting lines, 1 incineration plant (Kyiv, factory Energia) and 3 waste-fired facilities were in operation. In 2017 separate gathering of MSW was introduced at 822 small towns, in 2018 – at 1181. There exists in Ukraine 460 cities, 500 regions, 885 small towns and 28388 villages. Among all amount of gathered MSW – 94 % is a mixed waste.

Almost 95% of gathered MSW (10 – 11 mln t) in Ukraine is disposed on landfills. As of the end of 2018 Ukraine has 6107 landfills, incl. 256 is overloaded ones, 984 – don't meet safety conditions. Total area of landfills and dumps is about 9172.4 ha, area of landfills that don't meet safety – 1753.1 ha. Based on National strategy to manage waste in Ukraine till 2030, more than 99 % of landfills in operation don't meet EU conditions of Directive 1999/31/ЄС «On waste disposal». Beside this, more than 30 ths. non-permitted landfills are created annually. Based on MERT info in 2017, 30184 such landfills were formed occupying area more than 896,07 ha. Almost about 19.1 mln m^3 (3 626.4 ths t) of MSW was disposed in a non-permitted manner in 2017.

Besides this, one of the problem of MSW landfills disposal is biochemical decomposition of waste that results in dump gas formation that is consisted of greenhouse gas – CH4 (55–60 %) and CO2 [1]. Accumulation of methane in a body of landfill may lead to MSW self-ignition. Uncontrolled combustion is accompanied with formation of toxic compounds such as dioxins. According to the Intergovernmental Panel on Climate Change (IPCC. ch), landfill emissions contribute to 18% of the total methane emissions to the atmosphere, giving from 9 to 70 megatons annually. As the above mentioned, Law of Ukraine «On waste» forbids storage of untreated MSW. National strategy foresees to achieve by 2023 such targets: treatment of 15 % of MSW, separate gathering of MSW from 23% of population, and in 2030 – 50 % MSW and 48 % population correspondingly.

One of measures that allows both eliminate influence of MSW greenhouse gas decomposition in air, ground water and the environment contamination, biological stabilization of waste and significantly reduce the volume of waste (by 90 %) and weight (by 75 %) is incineration. MSW is the burning of waste in a controlled process within a specific plant that has been built for this reason. The primary objective of incineration is to reduce MSW volume and mass and also make it chemically inert in a combustion process avoiding additional fuel use (autothermic combustion). In addition it also gives recovery of energy, minerals and metals from the waste stream. Term «Waste-to-Energy» includes various types of technologies for treatment of waste to obtain energy as heat, electricity or as alternative fuel, thus, heat treatment of waste at waste-fired plants, production and combustion of RDF (Refuse Derived Fuel). Set of technologies «WtoE» is one of promising way to save organic fuel and decrease emissions of greenhouse gases. It is also an economically and ecologically sound method to ensure a renewable source for energy while diverting waste from landfills. Waste to energy is one of the robust energy options to reduce CO_2 emissions and replace fossil fuels. Approximately 2/3 of household waste is categorized as biomass. Therefore, we can recover 2/3 as CO2-neutral energy and reduce our dependence on fossil fuels.

Incineration follows separate gathering and/or sorting of MSW. Such components as paper, glass, plastics and metal go to recycling. Organic compounds – plants and rest of meals – are fed to composting or landfill. The rest wastes (almost one third of MSW) – is source for future fuel. It was pressed in briquettes or granules. Obtaining the Refuse Derived Fuel (RDF) is the process of removing the recyclable and noncombustible from the MSW and producing a combustible material, by shredding or pelletizing the remaining waste. Several types of RDFs can be made, such as coarse, fluffy, powdered or densified, depending on the composition of the refuse, and the technology used. The benefits of such approach are as follows: wastes becomes useful goods that can be accumulated, stored, transported.

Waste-to-Energy was traditionally widely used in countries having deficit of free area for waste disposal. Despite this, even in Australia in the Kwinana Industrial Area around 40 km south of Perth in 2018 it was started construction of first Waste-to-Energy plant with 36 MWe and annual capacity of 400 ths t of waste. Now in the world more than 2600 WtoE plants are in operation incl. 500 is in Europe, 100 plants in North America and 1600 in Asia. In Table 2 the number and productivity of WtoE plants working in EU are presented (Source: EUROSTAT 2019, Confederation of European Waste-to-Energy Plants (CEWEP). It is also given information on Norway and Ukraine. In EU in 2017 the part of MSW, that was burnt-out while energy re-involving, achieved 28.1% of total MSW amount, in Ukraine – just 2,2%. Now, according to CEWEP, W(MSW)toE plants in EU can provide with electricity about 19 millions of people and with heat about 16 millions people. In 2016 these plants produced 40mln kW· h of electricity and 93 mln kW·h of heat.

In USA, in 2016, 71 power plants generated about 14 billion kWh of electricity from burning about 30 million tons of combustible MSW, 12,8% of total amount of MSW in USA (as to U.S. Environmental Protection Agency). In USA more than 119 WTE plants are now in operation including those with direct combustion (mass burn and RDF): 100 plants – mass burn (burns/combusts everything), 19 – RDF combustion.

In Japan 45 mln t of MSW is annually formed. Japan is a world leader in implementing incineration technologies – more than 75% of MSW is burnt and among them more than 30% with electricity producing. Japan has about 1500 incineration plant, from which in Tokyo from 1983 to 2017 p. was put into operation 21 incineration plants (Table 3 as to Clean Authority of Tokyo).

Table 2

The amount of MSW, share of its combustion at incineration plants, EU, Ukraine and Norway plants performance in 2017

Country	MSW amount			Waste-to-Energy plants	
	Total,	Waste-to-Energy		Number	Capacity
	ths t	ths t	%*	Units	ths t/year
European Union - 28 countries	248655	69 953	28.1	487	91 660
Belgium	4659	2 002	43.0	18	3410
Bulgaria	3080	103	3.3	–	–
Czechia	3643	634	17.4	4	700
Denmark	4503	2 380	52.9	26	3470
Germany	52342	16 185	30.9	121	26000
Estonia	514	217	42.2	1	240
Ireland (in 2016)	2763	811	29.4	1	230
Greece	5415	58	1.1	–	–
Spain	21530	2 780	12.9	12	2880
France	34393	12 220	35.5	126	14400
Croatia	1716	1	0.1	–	–
Italy	29583	5 634	19.0	41	6210
Cyprus	547	2	0.4	–	–
Latvia	851	21	2.5	–	–
Lithuania	1286	236	18.4	1	260
Luxembourg	362	161	44.5	1	160
Hungary	3768	608	16.1	1	350
Malta	283	0	0.0	–	–
Netherlands	8787	3 901	44.4	12	7800
Austria	5018	1 944	38.7	11	2500
Poland (in 2016)	11969	2 922	24.4	5	500
Portugal	5012	974	19.4	4	1200
Romania	5325	227	4.3	–	–
Slovenia	974	111	11.4	12	2900
Slovakia	2058	197	9.6	2	290
Finland	2812	1 646	58.5	8	1470
Sweden	4551	2 400	52.7	34	5990
United Kingdom	30911	11 578	37.5	46	10700
Norway	3949	2 088	52.9	17	1610
Ukraine	11271	247	2.2	1	247

Despite incineration is by far the most widely applied, there are three main types of thermal waste treatment such as: incineration – full oxidative combustion (the most common process); gasification – partial oxidation; pyrolysis – thermal degradation of organic material in the absence of oxygen.

Combustion can be applied as mass burn (burns/combusts everything without pre-treatment) and RDF-burn, gasification as conventional gasification and plasma arc gasification. In accordance to BAT, pyrolysis and gasification are rarely applied for heat treatment of MSW and RDF. Grate (or Stoker-firing) incinerators are widely used for the incineration of mixed municipal wastes. In Europe approximately 90% of installations treating MSW use grates. Fluidized bed incinerators are widely applied to the incineration of finely divided wastes such as RDF.

The incinerators required by different waste-energy combustion ways (mass burn, RDF, incineration, gasification, pyrolysis) are markedly different, and so are their costs and environmental impacts. Mass burn is typically a low efficiency approach. While it eliminates large amounts of refuse, little energy is recovered. Typically, not sorted MSW has an average heating value of 8 to 12 MJ/kg, in comparison with 19 MJ/kg for dry wood, 15 MJ/kg for lignite or 22 MJ/kg for steam coal.

Waste-to-Energy plants are characterized by high CAPEX. According to Renewable Energy World company ranges for CAPEX for each of the thermal technologies assume a 15 MW output for a: direct combustion (Mass Burn and RDF) varies from $7,000 to $10,000 per kW; pyrolysis ranges from $8,000 to $11,500 per kW; conventional gasification varies from $7,500 to $11,000 per kW; plasma arc gasification ranges from $8,000 to $11,500 per kW. Costs vary from technology to technology due to each having unique design characteristics, variations in equipment costs, site specific waste characteristics and site space requirements. There are significant other factors that can negatively affect the costs of construction – location of plant in a city, limited construction, high architectural requirements etc. Now in Ukraine waste disposal at landfills remains the cheapest while high dirty way доf MSW management. Tax for MSW disposal in Ukraine is 4,5 UAH/t or 0,15 euro/t, but in Holland - 107, Belgium - 82, Finland – 70, Denmark - 65, Great Britain - 64, Sweden - 49, Poland - 27, Austria - 26, France - 20 euro/t (as to State Agency on Energy Efficiency and Energy Saving of Ukraine). The future of energy utilization of MSW in Ukraine will become feasible only when the waste disposal cost be higher its treatment/utilization.

In Ukraine the only one incineration plant is in operation Energia (Kyiv) having maximum annual capacity of 300 ths t of MSW. MSW is burnt at the temperature of 900–1000 oC. Plant can produce 227 ths Gcal of heat and up to 50,7 mln kW·h electricity per year. According to National strategy to manage waste in Ukraine it is planned to increase the level of thermal treatment of MSW up to 10% of total amount by means of construction of 19 heat treatment utilization plants for MSW. Composition of MSW is one of important parameters affecting the technology selection. According to National strategy average morphological composition of MSW in Ukraine is as follows: organic waste – 30%, cellulose-containing material (paper, cardboard, newspapers, wrapping etc.) – 17%; metals – 3%; polymers – 11%; glass, ceramics – 6%; hazardous waste – 1%, others – 32%. The share of waste having organic compound is 70–78%. Morfological composition of MSW significantly changes over the year seasons: in summer and autumn – the share of organic waste increases while in winter – non-organic waste dominates.

Table 3

Tokyo's Incineration Plants

Plant	Company producer, type*	Capacity, tons day x furnaces	Maximum heating value, kJ/kg	Power generation capacity, kW
Hikarigaoka	A, Mitsubishi Heavy Industries Environmental & Chemical Engineering Co., Ltd. (MHIEC)	150x2=300	11,3	4,0
Meguro	A, Nippon Kokan Corp	300x2=600	11,7	11,0
Ariake	A, MHIEC, reconstruction planned	200x2=400	14,2	5,6
Chitose	A, Kawasaki Sun	600x1=600	12,1	10,0
Edogawa	A, Nippon Kokan Corp	300x2=600	12,1	12,3
Sumida	A, Hitachi Zosen	600x1=600	13,0	13,0
Kita	A, MHIEC	600x1=600	12,1	11,5
Shin-Koto	A, TAKUMA-type HN	600x3=1800	13,4	50,0
Minato	A, MHIEC	300x3=900	13,4	22,0
Toshima	B, Ishikawajima-Harima Heavy Industries	200x2=400	13,4	7,8
Shibuya	B, Ebara Corporation Rotational flow	200x1=200	13,4	4,2
Chuo	A, Hitachi Zosen	300x2=600	13,4	15,0
Itabashi	A, Sumitomo W+E-type	300x2=600	12,1	13,2
Tamagawa	A, Ishikawajima-Harima Heavy Industries	150x2=300	12,1	6,4
Adachi	A, Ebara HPCC	350x2=700	12,1	16,2
Shinagawa	A, Hitachi Zosen	300x2=600	12,1	15,0
Katsushika	A, Takuma SN	250x2=500	12,1	13,5
Setagaya	C, Kawasaki Fluidized bed type	150x2=300	12,1	6,75
Ota	A, TAKUMA-type SNF type	300x2=600	14,8	22,8
Nerima	A, JFE	250x2=500	14,3	18,7
Suginami	A, Hitachi Zosen	300x2=600	14,3	24,2

*Incinerator types: A – Stoker furnace (Full continuance combustor), B – Fluidized bed furnace (Full continuance combustor), C – Gasification melting furnace (All continuous operation)

As to Kyiv, based on State-owned R&D and Design & Technological Institute of Municipal Economy, in 2011 average morphological composition of MSW was as follows: paper, cardboard – 13.24%, food and garden waste – 39.26%, plastics, PETF bottles and boxes, polymer film, TetraPak package – 10.23%, black and colored metals – 1.11%, tree – 1.35%, textile, skin – 2.79%, glass – 13.01%, hazardous waste – 0.01%, not-sorted combustible rest – 14.68%, not-sorted non-combustible mineral waste – 4,31%. Average ultimate and proximate analyses of Kyiv MSW: C^r = 16.54%, H^r = 2.36%, O^r = 13.69%, N^r = 0.54%, S^r = 0.13%, A^r = 18,2%, W^r = 39.03%, heating value – 6,2–6,3 kJ/kg. After selection of secondary feedstock at sorting line, water content increases up to 48.3%. In this case heating value of sorted MSW decreases till 5,4–5,5 kJ/kg and becomes too low for direct combustion. After selection of secondary feedstock and separation from waste mineral non-combustibles and organic components, capable of biological decay, water content of wastes decreases up to 25 %, and heating value increases to 10,4–10,5 kJ/kg. Such wastes are applicable for RDF production.

Limiting emissions in flue gases from energy plants including incineration ones should comply with Directive 2010/875/EC on industrial emissions (Table 4). It is seen that requirements of Directives 2010/75/EU significantly affect the thermal technology selection for MSW/RDF utilization and proper flue treatment.

Table 4.

Emissions requirements of Directive 2010/75/EC on industrial emissions

Substances, mg/Nm^3	Dust	TOC	HCl	HF	SO_2	NO_x	CO	Cd+Tl	Hg	Heavy Metals	Dioxins and Furans
Waste Incineration	10	10	10	1	50	200	50	0.05	0.05	0.5	0.1
Co-incin. in Cement Kiln	30	10	10	1	50	500	–	0.05	0.05	0.05	0.13

Conclusion

Based on the above mentioned the following recommendations and conclusions can be summarized as follows. The problem of optimal waste management is actual all over the world. The trends and obligations to manage waste in proper way are available worldwide becoming a part of leading countries national legislation. The main trend in leading countries assume that MSW should be separately gathering, further proper sorted, valuable components should be recycled and secondary refused fuel should also be derived and then utilized as much as possible. Waste disposal on landfills must be as little as possible while the principle of circulating economy should be deeply implemented. Great amount of energy can be derived from MSW in a form of RDF that can substitute limited fossil resources while using secondary fuel for electricity and heat production in environmentally sound manner. Ukraine faces a lot of issues concerning the proper waste management implementation both in legislation and technology introduction accounting for EU requirements on industrial emissions.

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Mathematical modeling of the dynamics of heat and mass transfer, phase transformations and thermal decomposition at high temperature drying of biomass

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A mathematical model and method for calculating heat and mass transfer, phase transformations and shrinkage during drying of colloidal porous bodies in the form of a final cylinder are presented. A mathematical simulation of high-temperature drying of willow accompanied by the destruction of hemicellulose was carried out using the data obtained on the values of the activation energy of various types of biomass.

Keywords – biomass, drying, thermal destruction, mathematical modeling, dynamics of heat and mass transfer, phase transformations, cylindrical particle, drum dryer, activation energy.

The use of biomass for the production of solid fuels has a high potential for the transition to renewable energy sources in Ukraine and in Europe. Emissions from combustion of biomass are recognized as CO_2-neutral. Quality fuel pellets are obtained from raw materials with humidity of 8 – 12%. In Ukraine, drying of crushed biomass is carried out mainly in drum driers at coolant temperatures Tc = 120 – 170 ºC. The organization of high-temperature (Tc = 300 – 500 ºC) drying of biomass intensifies the process and is accompanied by thermal decomposition of biomass. At the initial stage of thermal decomposition, hemicellulose decomposes with the release of oxygen-containing gases and pyrogenic moisture. This contributes to increasing the caloric content of biofuels. At temperatures above 270 ° C, cellulose and lignin begin to decompose, and these processes in the presence of air are exothermic for all types of biomass. Their passage contributes to the loss of the combustible component of biofuels. Consequently, the development of technologies for high-temperature drying of biomass is important for compliance with the condition of passing only the first stage of thermal decomposition. The possibilities of experimental methods for investigating high-temperature dehydration and thermal destruction in the particles of small size are substantially limited. More promising is the use of the method of mathematical modeling.

Biomass particles are colloidal capillary-porous bodies of cylindrical shape. Drying in high-temperature coolant involves the passage of heat and mass transfer through diffusion, filtration and phase transformations. Pyrogenetic water is removed along with residues of free and bound biomass moisture. The mathematical model [1] of dynamics of dehydration of biomass was based on the equation of transport of substance (energy, mass) [2]

$$c_{\text{ef}}\left(\frac{\partial T}{\partial t}+w_{\text{ef}\,r}\frac{\partial T}{\partial r}+w_{\text{ef}\,y}\frac{\partial T}{\partial y}\right)=\frac{1}{r}\frac{\partial}{\partial r}\left(\lambda_{\text{ef}}r\frac{\partial T}{\partial r}\right)+\frac{\partial}{\partial y}\left(\lambda_{\text{ef}}\frac{\partial T}{\partial y}\right)-LI_V, \tag{1}$$

$$\frac{\partial U_{\text{fl}}}{\partial t}+\frac{\partial(w_{\text{fl}\,r}U_{\text{fl}})}{\partial r}+\frac{\partial(w_{\text{fl}\,y}U_{\text{fl}})}{\partial y}=\frac{1}{r}\frac{\partial}{\partial r}\left(D_{\text{fl}}r\frac{\partial U_{\text{fl}}}{\partial r}\right)+\frac{\partial}{\partial y}\left(D_{\text{fl}}\frac{\partial U_{\text{fl}}}{\partial y}\right)-I_V-\frac{U_{\text{fl}}}{1-\varepsilon_V}\frac{\partial\varepsilon_V}{\partial t}, \tag{2}$$

$$\frac{\partial U_{\text{v}}}{\partial t}+\frac{\partial(w_{\text{g}\,r}U_{\text{v}})}{\partial r}+\frac{\partial(w_{\text{g}\,y}U_{\text{v}})}{\partial y}=\frac{1}{r}\frac{\partial}{\partial r}\left(D_{\text{v}}r\frac{\partial U_{\text{v}}}{\partial r}\right)+\frac{\partial}{\partial y}\left(D_{\text{v}}\frac{\partial U_{\text{v}}}{\partial y}\right)+I_V-\frac{U_{\text{v}}}{1-\varepsilon_V}\frac{\partial\varepsilon_V}{\partial t}, \tag{3}$$

$$\frac{\partial U_{\text{ai}}}{\partial t}+\frac{\partial(w_{\text{gas}\,r}U_{\text{ai}})}{\partial r}+\frac{\partial(w_{\text{gas}\,y}U_{\text{ai}})}{\partial y}=\frac{1}{r}\frac{\partial}{\partial r}\left(D_{\text{ai}}r\frac{\partial U_{\text{ai}}}{\partial r}\right)+\frac{\partial}{\partial y}\left(D_{\text{ai}}\frac{\partial U_{\text{ai}}}{\partial y}\right)-\frac{U_{\text{ai}}}{1-\varepsilon_V}\frac{\partial\varepsilon_V}{\partial t}. \tag{4}$$

Here U_{fl}, U_{v}, U_{ai} – volumetric concentrations of liquid, vapor and air phases; T – temperature; t – time; c_{ef} – effective heat capacity, $c_{\text{ef}}=c_{\text{s}}\rho_{\text{s}}(1-\Pi)+c_{\text{fl}}U_{\text{fl}}+c_{\text{v}}U_{\text{v}}+c_{\text{ai}}U_{\text{ai}}$; λ_{ef} – effective thermal conductivity, $\lambda_{\text{ef}} = \lambda_{\text{s}}(1-\Pi) + \lambda_{\text{fl}}U_{\text{fl}} / \rho_{\text{fl}} + \lambda_{\text{v}}U_{\text{v}} / \rho_{\text{v}} + \lambda_{\text{ai}}U_{\text{ai}} / \rho_{\text{ai}}$; w_{ef} – effective filtration rate, $w_{\text{ef}} = \left[w_{\text{fl}}\, c_{\text{fl}}U_{\text{fl}} + w_{\text{g}}\, (c_{\text{v}}U_{\text{v}} + c_{\text{ai}}U_{\text{ai}})\right] / c_{\text{ef}}$; w_{fl}, w_{g} – are the velocity vectors of the filtration motion of the liquid and gas phases, which, according to the Darcy law $w_{\chi} = -K_0K_{\chi} / \eta_{\chi} \nabla P_{\chi}$ (χ = fl, g), are proportional to gradient the phases ∇P_{fl} and ∇P_{g}; L is the heat of phase transformation.

The effective diffusion coefficient of the liquid D_{fl} was determined by the formula obtained by Nikitenko N.I. [3], and a pair of D_{v} - from the kinetic theory of gas:

$$D_{\text{fl}} = \gamma_D[\exp(A_D / RT) - 1]^{-1}, \quad D_{\text{v}} = D_{\text{ai}} = \gamma_{\text{v}}T^{3/2} / P_{\text{g}}, \quad \gamma_D, \gamma_{\text{v}} = \text{const.} \qquad (5)$$

Here A_D is the activation energy of the liquid molecules for the diffusion process.

The pressures of fluid P_{fl} and gas P_{g} are expressed in terms of the functions U_{fl}, U_{v}, U_{ai} and T. Volume fractions of the solid component Ψ_{s}, liquid Ψ_{fl} and gas $\Psi_{\text{г}}$ in porous body are defined: $\Psi_{\text{s}} = 1 - \Pi$, $\Psi_{\text{fl}} = U_{\text{fl}}/\rho_{\text{fl}}$, $\Psi_{\text{g}} = 1 - \Psi_{\text{s}} - \Psi_{\text{fl}}$, partial densities of vapor and air: $\rho_{\text{v}} = U_{\text{v}}/\Psi_{\text{g}}$ and $\rho_{\text{ai}} = U_{\text{ai}}/\Psi_{\text{g}}$, partial pressures of vapor $P_{\text{п}}$ and air $P_{\text{в}}$: $P_{\text{п}} = \rho_{\text{п}}R_yT/\mu_{\text{п}}$ and $P_{\text{в}} = \rho_{\text{в}}R_yT/\mu_{\text{в}}$. The pressures of gase and liquid phases: $P_{\text{g}} = P_{\text{v}} + P_{\text{fl}}$ and $P_{\text{fl}} = P_{\text{g}} + P_{\text{c}}$, where capillary pressure P_{c} [2]

$$P_{\text{c}} = 2\sigma(T) \int\limits_{r_{\min}}^{r_{\max}} \frac{\theta(r)}{r} f(r)dr \Big/ \int\limits_{r_{\min}}^{r_{\max}} \theta(r) f(r)dr = \frac{2\sigma(T)}{r^*}, \quad r_{\min} < r^* < r_{\max}. \qquad (6)$$

Here, $\theta(r)$ is the volume fraction of the capillary occupied by the liquid; $f(r)$ is the differential function of pore size distribution; $\sigma(T)$ is the coefficient of surface tension; r^* is the characteristic parameter of the dispersion of pore sizes; $r_{\min}$ and $r_{\max}$ are the minimum and maximum pore radii of a unit volume.

Intensity of phase transition on the outer surfaces of the biomass particles [4] is as the difference between the evaporating liquid streams and the condensed vapor

$$I = \gamma_{\text{c}}\left\{\varphi_{\text{b}}\big|_{\nu=0}\left[\exp\left(A / RT\big|_{\nu=0}\right) - 1\right]^{-1} - \varphi_{\text{e.m.}}\left[\exp\left(A / RT_{\text{e.m.}}\right) - 1\right]^{-1}\right\}, \ \gamma_{\text{c}} = \varepsilon\rho_{\text{fl}}\delta^*/4 \qquad (7)$$

where ε is the radiation coefficient; ρ_{fl} is the density of the liquid; δ^* is the thickness of the condensate layer in which the evaporation process takes place; φ_b is the body moisture, which is determined from the sorption isotherm equation, depending on U_{fl}; A is the activation energy; R is the universal gas constant; φ_{en} is the relative humidity of the medium, $\varphi_{\text{e.m.}} = P_{\text{v}} / P_{\text{eq}}$, P_{v} is the water vapor partial pressure, P_{eq} is the saturation pressure.

The expression for the intensity of evaporation I_V in the unit volume of the body follows from formula (6) under the condition of a local thermodynamic phase equilibrium

$$I_V = \gamma_V\left\{\left[\exp(A / RT - 1)\right]^{-1}\left[\varphi_{\text{b}} - \varphi\right]\right\}S. \qquad (8)$$

where φ is the relative humidity of the gas in the pores of the body, $\varphi = U_{\text{v}} / [\Psi_{\text{g}}P_{\text{sat}}(T)]$; S is the area of the contact surface of the liquid and gas phases. To determine the function S in pores of the unit volume of a body, which is not completely filled with liquid, the formula [5] was obtained

$$S = \frac{2\sqrt{1 - \varphi_{\text{b}}}}{\rho_{\text{fl}}\delta^*} \frac{\partial U_{\text{fl}}}{\partial \varphi_{\text{b}}}, \quad (S_{\min} \le S \le S_{\max}), \qquad (9)$$

where the derivative $\partial U_{\text{fl}}/\partial\varphi_{\text{b}}$ is found from the sorption isotherm equation. If the isotherm equation is given in the form $U_{\text{fl}} = U_{\max}\varphi_{\text{b}}^{\text{g}}$, g = const, then $\partial U_{\text{fl}} / \partial\varphi_{\text{b}} = U_{\max}g\varphi_{\text{b}}^{\text{g-1}}$. The data on the equilibrium moisture content W_{eq} for wood [6] accurately describes the equation $W_{\text{eq}}^{-1} = W_{\max}^{-1} - 0{,}12\ln\varphi$, $W_{\max}$ corresponds to φ=1 and at 100°C equals 16%, $U_{\text{fl}} = 0{,}01W\rho_{\text{b}}$.

Volumetric deformation ε_V was determined on the basis of the thermoconcentration deformation equation of Nikitenko N.I. [5], that was solved in [7] analytically for the case of an osseo-symmetric stressed cylinder state due to the heterogeneity of the temperature fields and the concentration of the components of the bound substance.

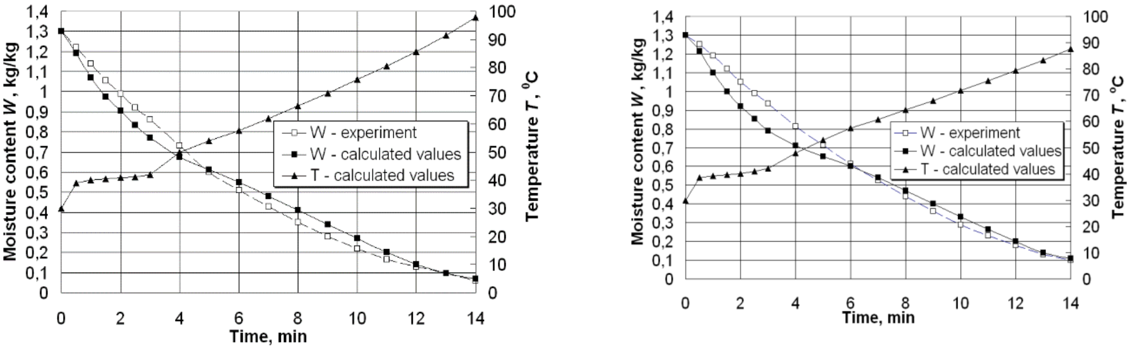
On the surfaces of the particles in contact with the drying agent, the boundary conditions of the heat-mass transfer of the third kind are given.

$$\lambda_{\text{ef}}\partial T/\partial\nu\big|_{\nu=0} = \alpha(T_{\text{e.m.}} - T\big|_{\nu=0}) - LI, \qquad D_{\text{fl}}\partial U_{\text{fl}}/\partial\nu\big|_{\nu=0} = I, \tag{10}$$

$$-D_{\text{v}}\partial U_{\text{v}}/\partial\nu\big|_{\nu=0} = \gamma_{\text{v e.m.}}\left(U_{\text{v}}\big|_{\nu=0} - \rho_{\text{v e.m.}}\psi_{\text{v}}\right), \quad U_{\text{ai}}\big|_{\nu=0} = \frac{P_{\text{v e.m.}}\psi_{\text{g}}\mu_{\text{ai}}}{R\;T\big|_{\nu=0}} - U_{\text{v}}\big|_{\nu=0}\frac{\mu_{\text{ai}}}{\mu_{\text{v}}}. \tag{11}$$

The solution of differential equations (1) - (4) under the conditions (10) - (11) was carried out by a numerical method developed on the basis of an explicit three-layer recalculated difference scheme of Nikitenko N.I. [5] and procedures for splitting the algorithm into physical factors. Difference approximation of the transfer equations (1) - (4) are presented in [1].

To confirm the adequacy of the mathematical model and the efficiency of the numerical method, a physical modeling of the kinetics of drying of energy willow particles of cylindrical form in the air flow and mathematical modeling of the process at the same initial data was carried out: $T_0 =$ 303 K; $W_0 =$ 1,3 kg/kg; $A = A_D =$ 0,4205·10^8 J/kmol; Π = 0,58. The results of the calculation and the experimental data presented in Figure 1 are well-coordinated.



a) b)

Fig. 1. Change in time of the average moisture content *W* and temperature *T* of energy willow of cylindrical particles with dimensions *d*/*h* = 4,2 /10 mm (a) and *d*/*h* = 5,6/10 mm (b) when drying in the air stream with the parameters: $T_{\text{e.m}}$ = 120 ° C, $w_{\text{e.m}}$ = 2 m/s, $d_{\text{e.m}}$ = 18 g/ kg s.ai.

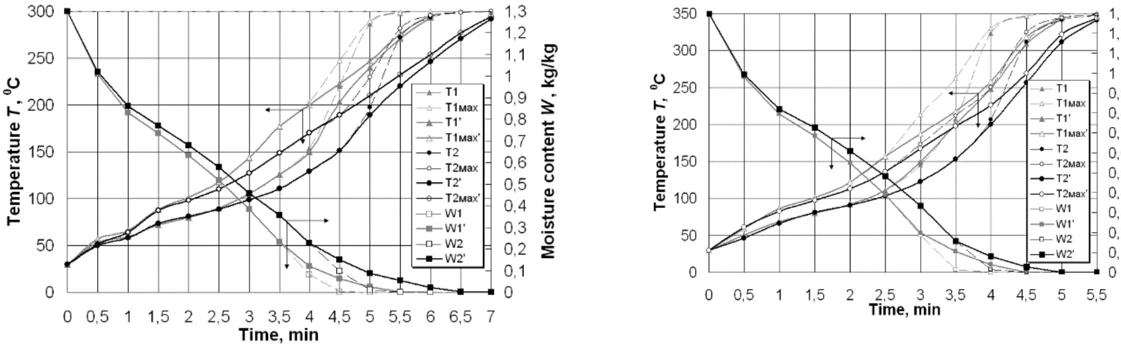
As shown in [8], the onset of the thermal decomposition of hemicellulose in the drying process of different types of biomass is characterized by a sharp change in the effective energy of activation of the microparticles of the bound substance. Some results obtained in [8] are given in Table 1.

Table 1

Effective activation energy at different stages of biomass dehydration

№	A sample of biofuels	Change of temperature of material, ºC	Activation energy, J/mol	Change of temperature of material, ºC	Activation energy, J/mol
1	Wheat straw	28-168/(87)	59300	168-318/(268)	93100
2	Trench of oak	23-190/(95)	51600	190-315/(300)	91300
3	Tern of poplar	28-183/(109)	59400	183-351/(311)	75250
4	Trench is pine	28-168/(85)	54900	178-335/(315)	10400
5	Miskanthus	28-180/(91)	57400	180-335/(284)	90500

Since the process of thermal decomposition, like diffusion and evaporation [5], is an activating, in mathematical modeling of joint processes of drying and thermal destruction in the calculation program developed on the basis of (1) – (4), in expressions (6), (7) and for D_{fl} after material temperature has reached the beginning of thermal decomposition, the value of the activation energy of water is changed to a value corresponding to the temperature interval of decomposition of hemicellulose [8] (Tab.1). For hardwood species of trees $A_{ef} = A_{Def} = 0{,}7525 \cdot 10^8$ J / kmol. Figure 2 shows the results of numerical experiments.



a) $T_{e.m}$ =300 °C b) $T_{e.m}$ =350 °C

Fig. 2. Change in time of the average moisture content W, temperature T, and maximum temperature T_{max} on the surface of energy willow particles in the sizes d/h = 5,6/10 mm (curve 1) and d/h = 5,6/10 mm (curve 2) at drying without and with taking into account thermal decomposition (W', T', T_{max}') in flue gases with parameters: $w_{e.m}$ = 2 m/s, $d_{e.m}$ = 18 g/ kg

Conclusion

The process of thermal decomposition, as well as the processes of diffusion and evaporation, is activating. Taking into account the mathematical model of this phenomenon will allow to organize the process of biomass drying effectively and improve the quality of biofuels.

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Coupling phytoremediation and biofuel production by using sea buckthorn

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Abstract* – *In this paper coupling phytoremediation and biofuel production by using Sea buckthornis given. Sea buckthorn brings many environmental benefits, including soil and water conservation, desertification control, land reclamation, erosion and water loss control, and the establishment of wild life habitats especially in fragile ecosystem due to its extensive root system coupled with efficient nitrogen fixation. Sea buckthorn has proved to be a popular green energy plant because of its quality biomass. It is a good source of firewood. The usage of Sea buckthorn oil is an effective biodiesel over other bio diesels formed from other vegetable oils.

Keywords – biofuel, phytoremediation, firewood, biodiesel, Sea buckthorn, *Hippophae rhamnoides* L.

Introduction

The world is confronted with the twin crisis of fossil fuel depletion and environmental degradation. Phytoremediation has been increasingly used as a more sustainable approach for the remediation of contaminated sites. The costs associated with this remediation method are usually lower than other well-known remediation technologies and some environmental impacts, like atmospheric emissions and waste generation, are inexistent. The biomass produced in phytoremediation could be economically valorized in the form of bioenergy (biogas, biofuels and combustion for energy production and heating), representing an important environmental co-benefit, added to others such as erosion control, improving soil quality and functionality, and providing wildlife habitat. Biomass-based energy is increasingly gaining popularity as a relatively clean, renewable and carbon-neutral alternative to fossil fuels. Coupling phytoremediation and biofuel production by using fast-growing species having bioenergy potential appears to be a rather attractive opportunity.

Results and discussion

We have found that Sea buckthorn is suitable for phytoremediation of oil-contaminated soils. Hippophae rhamnoides L. plants successfully adapt to adverse conditions of the oil-contaminated soils, improves physical, chemical and biological properties of soils, decrease their toxicity, reduce the amount of the contained oil, provide long-term phytoremediation and easily spread to unoccupied areas. The degree of soil cleaning from oil pollution reaches 92,7% [1].

Sea buckthorn is an ecologically and economically important plant that belongs to the family *Elaegnaceae*. The plant is hardy and it can withstand extreme temperatures from -40 ºC to 40 ºC. Sea buckthorn leaves are small, cuticle is thicker, crib-texture is well developed, leaf back densely covered with scales and star-hair to cover stoma. Seabuckthorn has a strong and well-developed tap root system, having primary, secondary and tertiary roots covered with root hairs. About 80% of its primary (feeding) roots are in the surface soil (0,2 to 0,8 m) which helps in preventing erosion. Sea buckthorn plantation intercepts precipitation by lush crown layer which redistribute precipitation and control surface runoff. Root nodules of H. rhamnoides have a symbiotic association with bacterium belonging to the genus *Frankia* having the ability to fix nitrogen from the air. It has been found that Sea buckthorn can fix upto 180 kg of nitrogen per ha per year, which generally improves soil fertility. They also transform insoluble organic and mineral matters from the soil to more soluble states. Plantation of Sea buckthorn improves soil physical characteristics and fertility thereby improves soil water holding capacity. It has been observed that soil moisture in Sea buckthorn plantation areas is 3-4% higher than outside the forest. Similarly air humidity is 10-20% higher in Sea buckthorn forest. The shrub has been found growing well in sandy, rocky, saline and ravine soils. Since it is resistant to drought and tolerates soil salinity and low temperatures, it is suitable for many situations that are simply too demanding for most plants. Thorny and bushy growth of Sea buckthorn provides a protective shelter for flora and fauna thereby maintaining the fragile ecosystem [1, 2].

Sea buckthorn has proved to be a popular green energy plant because of its quality biomass. It is a good source of firewood. In a six-year old Sea buckthorn forest, each hectare can produce 18 tons of firewood, equal to nearly 12,6 tons of standard coal [2]. The heat value of Sea buckthorn wood is 4785,5 kcal/kg, and so it can be used as a substitute for coal in various applications for burning.

Sea buckthorn oil is an good option for the manufacture of biodiesel. Biodiesel is an alternative energy source and could be a substitute for petroleum-based diesel fuel. Biodiesel burns clean, which results in a significant reduction of the types of pollutants that contribute to smog and global warming and emits up to 85% fewer cancercausing agents. Biodiesel refers to a vegetable oil or animal fat based diesel fuel consisting of long-chain alkyl (methyl, propyl or ethyl) esters. Biodiesel is meant to be used in standard diesel engines and is thus distinct from the vegetable and waste oils used to fuel converted diesel engines. Biodiesel can be used alone, or blended with petrol or diesel. It is found that the seabuckthorn oil is an effective biodiesel over other bio diesels formed from other vegetable oils. It has low viscosity among vegetable oils. Oils from Sea-buckthorn seeds and pulp differ considerably in fatty acid composition. While linoleic acid and α-linolenic acid are the major fatty acids in seed oil, sea buckthorn pulp oil contains approximately 65% combination of the monounsaturated fatty acid, palmitoleic acid, saturated fatty acid and palmitic acid [3].

Conclusion

In this paper coupling phytoremediation and biofuel production by using Sea buckthorn is given. The plant brings many environmental benefits, including soil and water conservation, desertification control, land reclamation, erosion and water loss control, and the establishment of wild life habitats especially in fragile ecosystem due to its extensive root system coupled with efficient nitrogen fixation. Sea buckthorn has proved to be a popular green energy plant because of its quality biomass. It is a good source of firewood. The heat value of seabuckthorn wood is 4785,5 kcal/kg. The usage of Sea buckthorn oil is an effective biodiesel over other bio diesels formed from other vegetable oils.

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Synthesis and investigation of dispersed metal oxide-graphene photoelectrode material

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Abstract* – *The technology of forming solar cells by layer-drawing of its components using the method of painting or spraying at room temperature is perspective to significantly reduce the cost of finished products. The goal of present work is to describe preparation and characterization of TiO_2, ZrO_2 – few layered graphene (FLG) composite materials for the fotovoltaic working electrode.

Keywords – photoanode material, graphene nanoparticles, composite electrode.

The uniform distribution of the conductive carbon phase between the semiconductor grains was provided by co-esterification of the ethanol dispersion of graphene particles and gel-like hydrated metal oxide from aqueous solutions upon a pH increase. The research was carried out by methods of electrochemical impedance and scanning electron microscopy[1]. To find the conductivity at the boundary between the grains (σ_{gr}), the Nyquist diagram is constructed in the coordinates Z "(Z) (Fig 1).

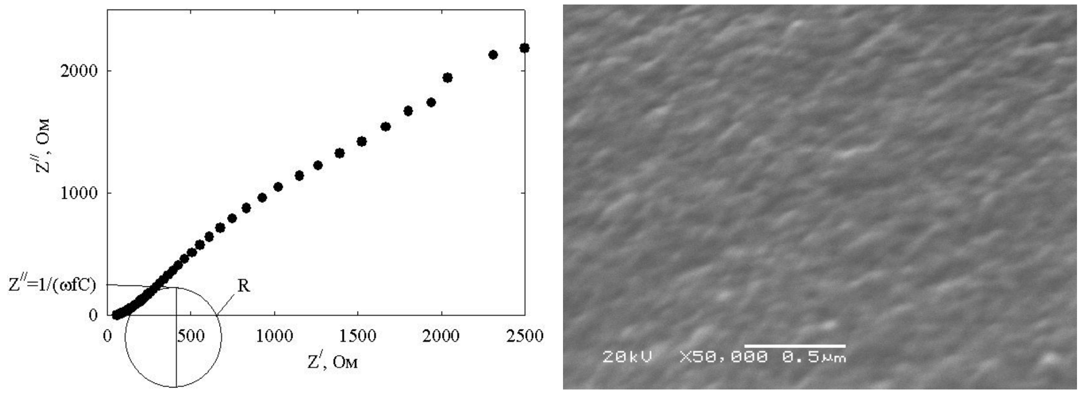

Fig 1. Nyquist diagram and SEM image of the FLG – semiconductor composite.

The circle position corresponds to the maximum on the admittance curve Y(*f*), where *f* is the frequency. The value σ_{gr} is estimated as 0.025 Ohm^{-1}m^{-1}. This value is ten times less than that of direct current σ_{dc}, which is typical for disperse samples.

The capacity of grain boundaries is 6.24×10^{-5} F. The high measured value σ_{dc} shows that the amount of graphene in the composite exceeds the percolation threshold. This indicates that graphene particles are in contact for the composite. The latter provides a continuous conductivity and promotes the charge transfer in the conposite.

Conclusion

The analysis of impedance spectra showed the presence of composite structures that are able to transfer and accumulate energy. The synthesized composites can be used as photoconductive materials for flexible solar cells.

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Improvements That are Applicable in the Automation System to Increase CH_4 Ratio in Co-Fermentation Plants

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Abstract – Increasing the rate of CH_4 in thebiogas is very important in terms of the efficient evaluation of the resources as well as the efficient fulfillment of energy demand. One of the methods that can be used for this purpose, also known as co-fermentation, is to process different organic wastes, at a certain rate. Although the fermentation of organic waste mixtures in the specified amounts contributes to the increase of the CH_4 ratio in the biogas content, it may cause the halt of biogas production in excess of the amounts determined in the organic waste mixture ratios. In this study, improvements in biogas plant automation are presented and proposed to prevent digester failure in plants producing biogas with co-fermentation.

Keywords – Biogas production, Programmable logic control, Biogas plant automation, Co- fermentation, İncreased methane content

Introduction

Nowadays, in parallel with the evolving living standards, increasing the amount of energy consumption and finding alternatives to fossil-based energy sources have significantly increased the interest in renewable and also sustainable energy resources. One of the renewable and sustainable energy sources, biogas production under anaerobic conditions (biometanation), in other words, production of methane (CH_4) from organic wastes, can be considered among the prominent sources of energy, due to the high potential of energy production as well as being considered as a helping factor in eliminating environmental problems. The biogas content produced by anaerobic fermentation includes a small amount of NH_3 (80-100 ppm), H_2S (1000-3000 ppm) and hydrocarbons (<100 ppm) and 55-70% CH_4, 30-45% CO_2 [1,2]. The lower thermal value of the biogas increases due to the increase in the methane content in the biogas content [3]. The Biogas has a Lower heating value of 20.5 MJ / m3 with a methane content of 57%, while the biogas with a methane content of 51% has a Lower heating value of 18.6 MJ / m3 at 1 atm and 15 ° C. Bigogaz can be used efficiently both in electricity generation (as fuel in generators) and in households for heating and cooking [4]. Anaerobic fermentation can be divided into four biological processes: hydrolysis, acidogenesis, acetogenesis, and methanogenesis [5,6]. Aneorabic fermentation is a complex biological process. In this process fermentation is influenced by both physical factors such as retention time, temperature, mixing, loading rate and chemical factors that are influencing the environment such as C / N, pH, alkalinity, toxic substances [7]. Organic wastes used in fermentation are an important factor in biogas production. Each organic material has the potential to produce a certain amount of biogas when appropriate conditions are met. The co-fermentation of different raw materials changes the biogas production potential and improves process efficiency according to mono-digestion (single organic waste fermentation) [8]. Kim at al. has co-fermented spent coffee ground with sea lettuce and food waste due to the fact that the spent coffee ground is prone to fermentation failure when subjected to fermentation process alone. In addition, they determined the optimum ratio of waste used in co-fermentation for high methane yield [9]. In their study, al-Mashad and Zhang reported that co-fermentation of food waste and dairy farm manure gave higher biogas yield results than dairy farm manure fermentation only by itself [10]. There are many research studies indicating the benefits of co-fermentation of different organic wastes [11-15]. In the literature, many studies related to co-fermentation of animal manure or wastewater with agricultural food can be found. In these studies co-fermentation was performed by adding two or three raw materials into the fermentor [16-22].

Co-fermentation can improve fermentation performance by providing stability of fermentation, adjustment of carbon / nutrient ratio, remedying the trace-element deficiency, reduction of inhibitory content, increasing the buffering capacity [9,23]. Therefore, the selection of the appropriate raw materials to be fermented together and the determination of the optimum mixing ratios are very important for successful fermentation [9]. Although the fermentation of organic waste mixtures in the specified amounts contributes to the increase of the CH_4 ratio in the biogas content, it may cause the biogas production to halt in excess of the amounts determined in the organic waste mixture ratios. Although the fermentation of organic waste mixtures in the specified amounts contributes to the increase of the CH_4 ratio in the biogas content, it may cause the halt of biogas production in excess of the amounts determined in the organic waste mixture ratios.

In this study, in order to prevent fermentation failure and to increase the methane yield, a biogas plant automation was proposed in which pneumatic actuator, solenoid valve, flowmeter, lobe pump was used, to the plants producing biogas with co-fermentation.

Proposed system

Facilities with anearobic fermentation process are generally divided into four processes, although there are facilities in different operating styles. These are process 1 fermenters; process 2 production of biogas; process 3 evaluation of biogas; and process 4 evaluation of fermentation wastes. Figure 1 shows the general process for biogas production [24].

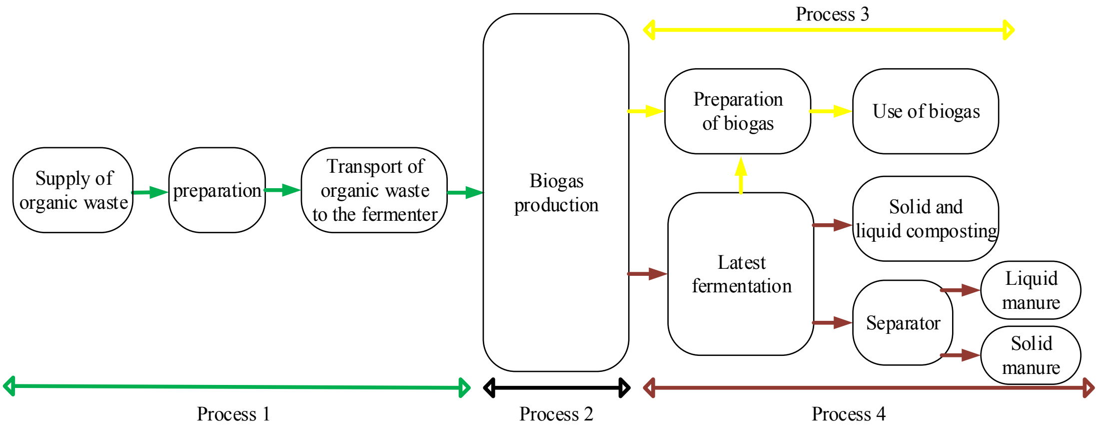


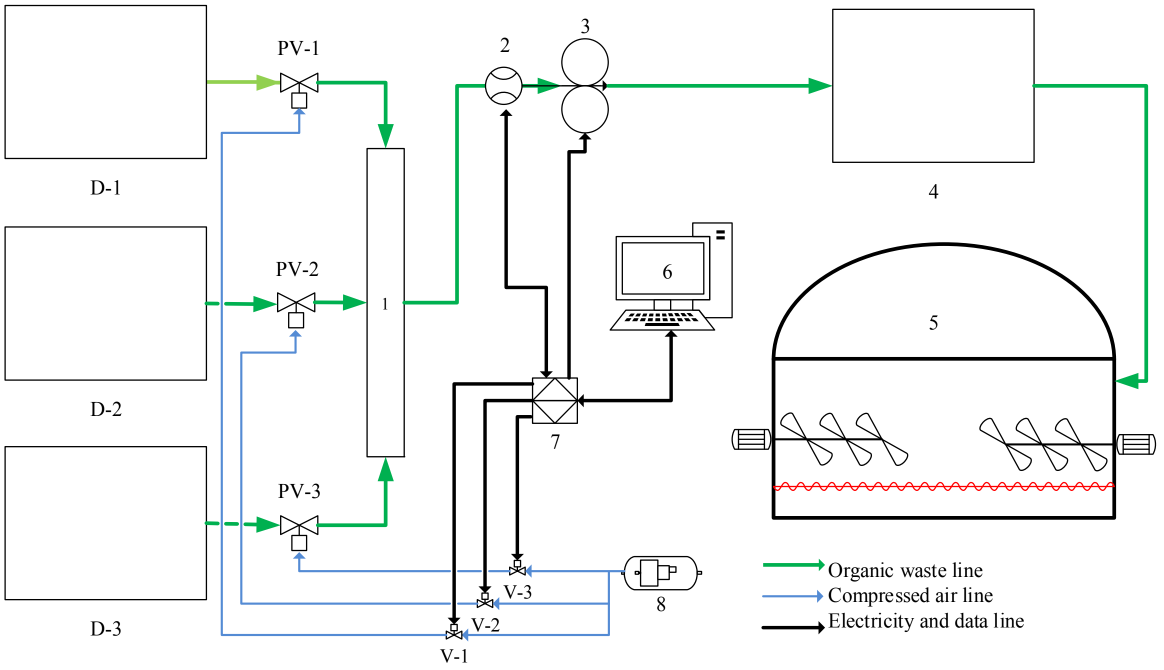
Figure 1. General process for biogas production

The 1st process consists of the procurement of organic raw material, fragmentation and crushing of the raw material if necessary, and the addition of organic raw material to the fermenter.

Generally, the transportation of the raw material in the plant and the feed of the fermentor is carried out by machines such as loader or bulldozer. 2nd process is the production of biogas in the fermenter. The 3rd process consists of the use of the produced biogas in cogeneration or trigeneration systems. The 4th process is related to the processing of the fertilizer after fermentation.

Traditionally, in biogas plants that work with different wastes, work of transportation of organic wastes to the mixing tank for the co-fermentation, is carried out by a loader or similar heavy duty vehicle. If optimum mixing ratios cannot be achieved in the mixing tank, the methane production rate decreases.

In the proposed system, optimum mixing ratios will be obtained by ensuring that the organic raw material is sent automatically to the mixing tank at the determined rate from the tanks made for the different mixtures. Thus, the increase in methane production can be realized at maximum level. Figure 2 shows a diagram of the proposed system.



D	Organic waste storage	4	Mixing tank
PV	Knife gate valve with pneumatic actuator	5	Fermenter
V	Convertible solenoid valves	6	Computer
1	Organic waste collector	7	Programmable logic controller
2	Flowmeter	8	Air compressor
3	Lobe pump		

Figure 2. Schematic view of raw material transfer system,

The system is designed to pump the set values to the mixer. The amount of waste to be sent to the mixer from the D-1, D-2 and D-3 organic waste tanks is entered from the scada screen. PLC triggers the pump and the convertible solenoid valve for organic waste delivery from the D-1 organic waste tank to the mixer, the compressed air through the V-1 valve opens the PV-1 valve and the organic waste transfer from the D-1 to the mixing tank takes place. The flow meter on the line sends the passed amount as a signal to the PLC. Valves and pumps close when the set value is reached. When the value set in the Scada display is reached, the valves and pumps are switched off. The same process is repeated in organic wastes stored in D-2 and D-3 tanks, thus ensuring optimum mixing ratio to the Mixing tank and so the optimum mixing ratio is provided to the Mixing tank.

Conclusion

Increasing the rate of CH_4 in thebiogas is very important in terms of the efficient evaluation of the resources as well as the efficient fulfillment of energy demand. One of the methods that can be used for this purpose, also known as co-fermentation, is to process different organic wastes, at a certain rate. Although the fermentation of organic waste mixtures in the specified amounts contributes to the increase of the CH_4 ratio in the biogas content, it may cause the halt of biogas production in excess of the amounts determined in the organic waste mixture ratios. Therefore, the selection of the appropriate raw materials to be fermented together and the determination of the optimum mixing ratios are very important for a successful fermentation. In this study, improvements in biogas plant automation are presented and proposed to prevent digester failure in plants producing biogas with co-fermentation.

In this study, it is suggested to the plants which are producing biogas with co-fermentation, make improvements in automation by adding organic waste storage, knife gate valve with pneumatic actuator, organic waste collector, flowmeter, lobe pump, to prevent digester failure and to achieve maximum methane yield.

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Microhardness of the amorphous and nanostructured alloys system Al_{87} (Y, Gd)$_5Ni_8$ as electrodes for hydrogen evolution

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It was investigated the processes of hydrogen evolution on aluminum amorphous and nanostructured electrodes $Al_{87}Y_5Ni_8$, $Al_{87}Y_4Gd_1Ni_8$, $Al_{87}Gd_5Ni_8$ in 1 M KOH alkaline solution. By electron microscopy method it was analysed the electrodes surface and found elemental composition before and after hydrogen evolution reaction in alkaline environment. It was also explored mechanical properties of AMA-electrodes before and after hydrogen evolution reaction. The main purpose of the research work was to find new electrode materials for hydrogen power engineering.

Keywords: amorphous metallic alloys, nanocrystals, microhardness, hydrogen evolution reactions

Introduction

The properties of the amorphous metallic alloys (AMA) are determined by the nature of the base metal, as well as the composition of alloying additions. Therefore, changing the elemental composition of the AMA it could be expanded the field of their applicability. The amorphous metallic alloys based on aluminum and alloyed with transition and rare-earth metals (RE) can demostrate catalytic action in various oxidation-reduction processes, including the hydrogen evolution reactions, while maintaining a high level of corrosion [1, 2]. The purpose of the research work was to investige electrochemical hydrogen evolution reactions from alkaline solutions by the Al-based amorphous alloys doped with Y and Gd.

Widely researched scientific problem – the hydrogen synthesis and accumulation by AMA alloys. Electrochemical hydrogen synthesis can be adjusted by changing the electrode composition, electrolyte concentration, temperature change of the electrochemical system [3, 4]. Promised for hydrogen evolution reactions are high resisted in aggressive environment amorphous metallic alloys, so they can be used as hydrogen allocation electrodes in corrosive solutions in wide range of pH. An important direction is the hydrogen accumulation, which takes place on the cathode in case of metallic hydrides formation [5].

The AMA are corrosion resistant in media with pH close to neutral, but electrodes based on Al are dissolving in strong alkaline and acidic aqueous solutions resulting in hydrogen evolution reactions [3-4]:

$$2Al + 6H_2O + 6OH^- = 3H_2 + 2[Al(OH)_6]^{3-}$$

$$2Al + 6OH_3^+ + 6H_2O = 3H_2 + 2[Al(OH_2)_6]^{3+}.$$

The homogeneous structure of the surface of amorphous alloys contributes to the formation of non-defective protective films and, thus, causes a high chemical resistance [6].

Experimental details

We investigated the chemical activity of amorphous metallic alloys based on Al: $Al_{87}Y_5Ni_8$, $Al_{87}Y_4Gd_1Ni_8$, $Al_{87}Gd_5Ni_8$. The electrodes were obtained by rapid hardening of the melt on the surface of copper drum rotating at high speed (10^6 K/sec). The electrochemical investigations were carried out in 1 M KOH aqueous solution. The AMAs were obtained at the G.V. Kurdyumov Institute for Metal Physics of the Ukrainian National Academy of Science (Kyiv).

The AMA was investigated using differential scanning calorimetry (DSC) with a heating rate of 10 K/min at the Silesian University Institute of Materials Science with the use of Perkin-Elmer Pyris 1. It is known [7] that in the temperature range of the first DSC maximum, the nanoscale AMA is carried out. From the DSC curves, the temperature of origin (T_1), growth (T_2) and the formation of α-Al (T_3) nanocrystals were determined [8].

Table 1 Temperatures (T ± 5K) of phase transitions of Al-based amorphous alloys

AMA	T_1, K	T_2, K	T_3, K
$Al_{87}Y_5Ni_8$	491	501	532
$Al_{87}Y_4Gd_1Ni_8$	441	456	503
$Al_{87}Gd_5Ni_8$	458	474	510

Thermal treatment of AMA in an oxygen-enriched medium with a heating rate of 10 °K/min to predetermined temperatures was carried out. For the electrochemical hydrogen evolution investigations of amorphous metallic electrodes we used three-electrodes scheme: AMA-electrode|1 M aqueous KOH|Ag/AgCI/KCl. For the attainment of the hydrogen release in thermostate cell at 293± 1°K during 30 min we used stationary potential E = -1,2 V and Jaissle Potentiostat/Galvanostat IMP 88PC-R.

The microhardness of AMAs was investigated by Vickers' method on the PMT-3 device before and after the hydrogen evolution reaction on aluminum amorphous and nanostructured alloys. The morphology of AMA surface was studied by the scanning electron microscopy. The microphotographs of the surfaces of the amorphous strips were taken by a scanning electron microscope REMMA-102-02 [9].

Results and discussion

Amorphous and nanostructured electrodes $Al_{87}Y_5Ni_8$, $Al_{87}Y_4Gd_1Ni_8$, $Al_{87}Gd_5Ni_8$ were investigated by the voltammetric method in the potentiodynamic mode. It was established the potential of hydrogen release E = -1.2 V, which is independent from the composition of the AMA-electrode.

From the dependence of the current density from time at E = -1.2 V, the volume of hydrogen released by the AMA electrodes in the 1 M KOH solution was calculated (Table 2). From table 2 it is seen that the largest volume of released hydrogen was on the AMA-electrode doped by Y and Gd.

An important characteristic of the AMA-electrodes in electrochemical hydrogen evolution reactions is the resistance to hydrogen overstress [10]. That's why it was necessary to investigate the microhardness of amorphous and nanostructured alloys before and after use them as H_2-electrodes. Results of microhardness measurements are given in Table 2. The highest microhardness have alloys dopped only by Y or Gd. Microhardness due to annealing increases. At T_3 which corresponds to the total formation of nanocrystals, increases to 3.9±0.5 GPa. This is due to the fact that after the first stage of crystallization Al nanocrystals are formed. X-ray structural analysis of samples showed that in all cases the Al lattice period is higher than in pure Al (0.40494 nm), which may indicate the formation of a solid Al(R) solution [8]. Based on the X-ray data obtained, the size of the Al(R) crystals after the heat treatment at T_3 was calculated by the Hall method [11]. The results of such calculations are presented in Table 3.

Table 2

Microhardness of Al-based amorphous alloys before and after the hydrogen evolution reaction in alkaline environment.

AMA	Heat treatment	V_{H2}, mL/cm^2·min	H_{v1}, GPa	H_{v2}, GPa
$Al_{87}Y_5Ni_8$	–	0,39	3,52	3,12
	T_1	0,55	3,83	3,3
	T_2	0,35	3,65	3,41
	T_3	1,02	3,88	3,6
$Al_{87}Y_4Gd_1Ni_8$	–	0,65	3,23	1,81
	T_1	1,17	2,46	1,58
	T_2	0,97	2,66	1,73
	T_3	0,7	2,97	1,92
$Al_{87}Gd_5Ni_8$	–	0,22	3,27	2,58
	T_1	0,82	3,42	2,18
	T_2	0,37	3,87	1,95
	T_3	*	3,93	*

H_{v1} – microhardness before the hydrogen evolution reaction;
H_{v2} – microhardness after the hydrogen evolution reaction;
* – the sample couldn't stand the conditions of the experiment.

The crystallite sizes calculated from the X-ray diffraction analysis are close to those obtained by electron microscopy (Table 3).

Table 3

Temperature of annealing (T_3) and averaged diameter (D) selected Al nanocrystals after the first stage of AMA crystallization.

№	AMA	$T_{annealing}$ ± 1, K	D, nm
1	$Al_{87}Y_5Ni_8$	532	20 ± 4
2	$Al_{87}Y_4Gd_1Ni_8$	503	9 ± 2
3	$Al_{87}Gd_5Ni_8$	510	15 ± 3

The results of electron microscopy of the $Al_{87}Y_4Gd_1Ni_8$ alloy are shown on Fig. 1. The microphotography proofs the amorphous state of the inial alloys. There are dark grains of Al(R), the light and gray regions of the amorphous matrix, which may be due to the different distribution of REM and Ni within it. This is evidence of the structuring of amorphous matrix after initial crystallization of Al(R).

The size of Al(Y) or Al(Gd) nanocrystals of 15 and 20 nm leads to an increasing of microhardness. The simultaneous presence of Y and Gd inhibits the growth of nanocrystals to a size of 9 nm, which leads to an increasing of the free volume in the amorphous matrix and to microhardness decreasing.

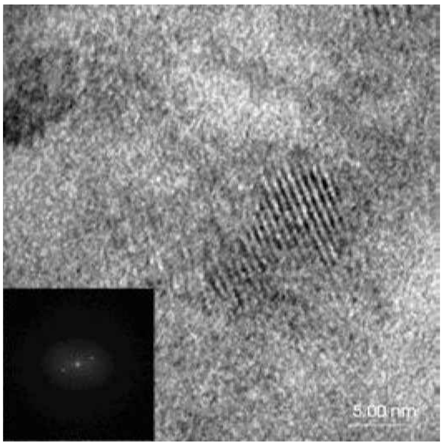

Fig. 1 Microstructure of $Al_{87}Y_4Gd_1Ni_8$ AMA annealed at 503 K [8].

AMA electrodes were investigated by scanning electron microscopy [9]. From the SEM photos it could be seen that the surface of the alloys becomes fragile after the processes of hydrogen evolution. Cracking degree depends on the elemental composition of the samples. Partial replacement of yttrium on gadolinium leads to an increasing in the stability of the electrodes to mechanical cracking. Similar results are described in [10].

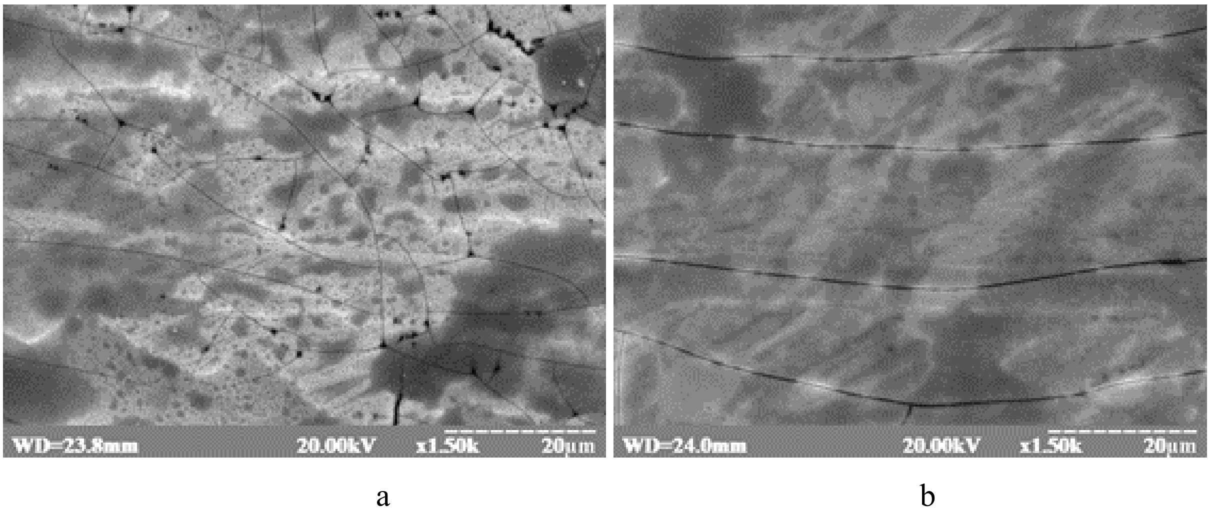

Fig. 2 SEM photos of the annealed (T_3) surface and after using AMA electrodes $Al_{87}Y_5Ni_8$ (a) and $Al_{87}Y_4Gd_1Ni_8$ (b) in the electrochemical hydrogen evolution reaction during 30 min in the 1 M KOH aqueous solution.

Investigation of microhardness of the AMA electrodes after an electrochemical reaction indicates a decrease in their mechanical strength. This is due to the dissolution of Al from the surface of the electrodes [10], both before and after heat treatment. The elemental composition of aluminum amorphous alloys before and after annealing at temperatures T_1, T_2, T_3 and subsequent hydrogen evolution during 30 minutes from 1 M KOH solution is presented in Table. 4. The results of the AMA surface investigation by the X-ray energy-dispersive spectroscopy showed that the content of Y, Gd and Ni increaseds on the surface (Table 4).

From the microphotographs it could be seen (Fig. 2) the two colored zones which were formed on the surface. Alloying only by yttrium creates finely dispersed areas on the surface of the AMA electrodes. The combined alloying by Y and Gd results in the formation of long dark-colored regions enriched with Ni atoms.

Table 4

Elemental composition of the AMA electrodes annealed and used in the electrochemical hydrogen evolution reaction (30 min), E=-1,2 V in 1M KOH

AMA	Heat treatment	V_{H2}, mL/cm^2·min	Elemental composition, at %			
			Al	Y	Gd	Ni
$Al_{87}Y_5Ni_8$	–	0,39	14, 77	12,99	—	24,75
	T_1	0,55	19,58	12,45	—	22,20
	T_2	0,35	43,39	9,84	—	21,80
	T_3	1,02	26,80	12,24	—	34,17
$Al_{87}Y_4Gd_1Ni_8$	–	0,65	24,02	11,54	16,26	13,09
	T_1	1,17	11,93	13,53	3,60	44,17
	T_2	0,97	19,28	11,08	3,37	38,04
	T_3	0,7	13,81	11,73	3,31	22,98
$Al_{87}Gd_5Ni_8$	–	0,22	20,28	—	16,14	24,19
	T_1	0,82	21,72	—	14,68	22,44
	T_2	0,37	23,87	—	14,11	30,52
	T_3	*	*	*	*	*

* – the sample couldn't stand the conditions of the experiment

Conclusion

Analyzing the research results, it can be seen that the $Al_{87}Y_5Ni_8$ alloy during heat treatment at the temperature T_3 (stable nanocrystallization) produces a sufficiently large amount of hydrogen - 1.02 mL/cm^2·min and has the highest microhardness of 3.6 GPa. The $Al_{87}Y_4Gd_1Ni_8$ alloy at the T_1 temperature (nanocrystals origin) produces the largest amount of hydrogen - 1.17 mL/cm^2·min among the investigated samples, however, its microhardness is 1.58 GPa much less than in case of the $Al_{87}Y_5Ni_8$ alloy.

By the method of electron microscopy it was shown that due to the electrochemical hydrogen evolution reaction from the 1 M KOH solution, an overstress of the surface of aluminum amorphous alloys is observed. It was established that on the surface of the electrodes the amount of Y, Gd and Ni increases as a result of dissolving Al in an alkaline solution. The volume of released hydrogen increases with an increase of Ni content during aluminum dissolution from the surface of AMA electrodes.

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ECOLOGY AND SUSTAINABLE DEVELOPMENT. ENVIRONMENTAL PROTECTION

Exposure to Selected Air Pollutants in the Grilling Process

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Abstract – Epidemiological evidence indicate that exposure to polycyclic aromatic hydrocarbons (PAHs) consumed with grilled meat might be hazardous for health. We used 3 different types of grills. 16 PAHs congeners were measured. PAHs exposure to charcoal briquettes incineration products might be even 10 times higher than in case of other types of barbecues.

Keywords – Barbecue, grill, lump charcoal, charcoal briquettes, propane, electric grill, inhalation exposure, particulate matter, polycyclic aromatic hydrocarbons, Monte Carlo simulation.

Introduction

Epidemiological evidence indicate that exposure to polycyclic aromatic hydrocarbons (PAHs) consumed with grilled meat might be hazardous for human health. In scientific literature however there is still lack of data concerning inhalation exposure to those compounds which are present in the barbecue exhausting gases. First investigation, made 2 years before, indicated that the inhalation cancer risk of the grill master could reach the level of $7.01\text{-}8.68\times10^{-1}$, which is on the unacceptable level. The main goal of the present analysis was to confirm the results of the first investigation and assess the possible cancer risk from the exposure to PM-bound PAHs generated during barbecuing, not only in the grill master but also people staying nearby the grill, witnessing the grilling process. The comparison of the risk, which can be experienced during the grilling process depending on the type of grill and fuel used for its powering, will also be presented. Alimentary and dermal risk has also been considered, however the results of the inhalation risk assessment will only be presented.

Materials and methods

The investigation was completed with the use of 3 different types of grills: a traditional one powered by two different types of fuels: lump charcoal (LC) and charcoal briquettes (CB) as well as the grill powered by liquid propane (LP) and electric energy (E). In case of each grill and fuel the exposure for PAHs and VOCs (BTX) of a grill master and other people has been investigated. Appropriate samples has also been taken in the control area, which was located in a certain distance from the grill position. In each case 3 separate types of samples has been collected: during the combustion of fuel itself (except the electric grill) and then while grilling vegetables and meat dishes.

The measurement was carried out using Gilian GilAir5 aspirators equipped with SKC Higgins-Dewell samplers and quartz filters. 3 of the aspirators were located above the barbecue hearth, 3 other in the control area and the other 3 were used as personal samplers to assess the individual exposure of people participating in the grilling process. In all of these three locations one of the sampler were equipped with an adsorbent for the extraction of polycyclic aromatic hydrocarbons (PAHs) in the gas phase, one in a previously weighed quartz filter that was designed to separate from exhaust gases the respirable particulates (PM_4) containing PAHs and the last one equipped with an adsorbent for the extraction of benzene, toluene and xylene (BTX). We focused on the respirable fraction due to its significant influence of health.

The results of PAHs in the PM_4 assessment will be presented. In the normal course of grilling PM_4 has been collected. Than 16 polycyclic aromatic hydrocarbon (PAH) congeners were extracted from PM samples and measured quantitatively using GC chromatograph. Result has been calculated for each of the three measurement cycles: the first one using empty grills, i.e. without food, the second with vegetables and the third one with meat dishes (identical set of food was placed on each type of grill). Data concerning PAHs contents in PM was further used to calculate its size dependent deposition in different compartments of human respiratory tract using multiple path particle dosimetry (MPPD) model. Finally a probabilistic risk model was developed to assess the incremental lifetime cancer risk (ILCR) faced by people exposed by breathing to carcinogenic PAHs.

Results

Using the electric grill and combustion of gaseous fuel (not containing polycyclic aromatic hydrocarbons) in the temperature at the level of about 200°C was rather less favorable for PAHs formation in comparison to the traditional grill powered by charcoal and especially charcoal briquettes. The effects of fuel/grill type on the formation of 16 different PAHs indicate a significant increase in PAHs concentrations in case of grill powered by charcoal briquettes. The total concentration of PAHs (over the barbecues hearths) ranged from 1652.1-1704.9 $\mu g/m^3$ in case of electric grill and 1087.2-5558.5 $\mu g/m^3$ in case of gas grill to 1538.8-19952.2 $\mu g/m^3$ in case of grill powered by lump charcoal and 13837.6-79561.9 $\mu g/m^3$ in case of grill powered by charcoal briquettes.

The daily exposure doses of PM_4 bound-BaP_{eq} for typical grill master while preparing food varies from 92-118 ng/day for E and 121-142 ng/day for LP to 124-204 ng/day for LC and 1022-1121 ng/d for CB. The effect of exposure to PAHs emitted from charcoal briquettes is therefore even 9-12 times higher than in case of electric grill and 7-9 times higher than in case of gas grill. The inhalation-ILCR followed a lognormal distribution with a geometric mean of 2.99×10^{-2}-2.71×10^{-1} in case of exposure to PM_4-bound PAHs emitted by unloaded grills, 6.40×10^{-2}-5.54×10^{-1} while grilling vegetables and 4.98×10^{-2}-6.08×10^{-1} when grilling meat. The highest values concern the grill powered by charcoal briquettes. The risk in personal exposure of people participating in the grilling process but not being a grill master varies in the range of 1.55×10^{-2}-2.52×10^{-2} and in the control area in the range of 5.33×10^{-3}-8.61×10^{-3}.

The risk for people who inhaled barbeque emission gases for 1,5 hours a day and 20 days a year in the period of 20 years exceeded 10^{-3} (which is the US Environmental Protection Agency non-acceptable level), suggesting high probability of cancer occurrences due to PAHs exposure.

Conclusion

The investigation shows that generally grilling process and especially using charcoal briquettes is dangerous concerning inhalation exposure to PAHs from barbecue exhausting gases. It was also observed that the exposure during preparing meat dishes is higher than in case of grilling vegetables. To protect against such risks it is recommended to use grill relatively rare and with the minimization of time spending over the barbecue hearth as a grill master. This kind of exposure could be highly dangerous for people occupationally exposed to barbecue exhausts.

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Impact of Physico-Chemical Properties of Transition Metal Oxide Based TiO_2 Catalysts on the Low-Temperature Selective Catalytic Reduction of NO by NH_3

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Abstract* – *The relationship between catalytic activity, redox behavior, acidity and NO_x adsorption ability of MO_x/TiO_2 (M: Co, Cu, Ce, Fe, Ni and Mn) catalysts was investigated for the low-temperature selective catalytic reduction of NO_x in the presence of NH_3.

Keywords – selective catalytic reduction, NO_x, transition metal oxides

Introduction

Nitrogen oxides (NO_x) are hazardous gases that cause problems such as photochemical smog, formation of fine particles, acid rain, ozone depletion and act as of greenhouse gases to the environment. Today, selective catalytic reduction (SCR) using ammonia is the most widely used technology for removal NO_x emitted from stationary sources, such as coal fired power plants and gas turbines. V_2O_5-WO_3/TiO_2 (VWT) catalysts have been commercialized for SCR and operate under moderate temperatures of about 320-450°C. However, some problems are still evident with the use of this catalyst: V oxide is highly toxic and successive dust pollution of the catalyst will eventually result from the upstream flue gas, which can cause the deactivation of VWT catalyst at the low temperature operation window (150-250 °C) [1]. In this temperature range MnO_x based catalysts supported on titania dioxide are suitable for the NH_3 system and possess excellent SCR activity [2]. Additionally, this catalytic system cause also very high yield of N_2O as a undesired product of the NH_3-SCR reaction. The impact of transition metal oxide (TMO) on the behavior of SCR catalysts is still not fully understood [1,2].The present study focuses on the investigation of the effects of TMOs by comparing the SCR activity and physico-chemical properties for catalysts with identical molar ratio of M:Ti.

Experimental

A series of Mn, Fe, Cu, Ce, Co and Ni oxide catalysts supported on TiO_2 (Anatase, P25) were prepared by wet impregnation. The content of active metal was kept at a constant molar ratio of M:Ti = 0.4 The prepared catalysts were characterized by XRD, N_2-sorption, H_2-TPR, NO_x- and NH_3-TPD. The activity of the catalysts for NH_3-SCR was studied using a model gas containing 500 ppm NO, 575 ppm NH_3 and 4 vol.-% O_2 in a fixed-bed flow-reactor in a temperature range of 120-400 °C and at a GHSV of 30,000 h^{-1}. The gaseous products were continuously analyzed by on-line NDIR-spectroscopy.

Results and discussion

The SCR studies show that Mn- and Cu/TiO_2 catalysts exhibit a high NO-conversion of 85-95 % at 180 °C (Fig.1a). However, a significant formation of N_2O with a yield of about 78 % was observed for Mn/TiO_2. In comparison, the yield of N_2O on Cu, Fe, Co, Ce and Ni containing catalysts was about 7-10 times lower, although at a lower NO_x-conversion of 40-65 %. The dependence of the NO_x-conversion on the TMOs for the catalysts follows the order: Mn > Cu > Co > Ni >Fe > Ce. NH_3-SCR, H_2-TPR, NO-TPD and NH_3-TPD results show a strong correlation between the ability of the TMO containing catalysts for the oxidation of ammonia, its catalytic activity and the yield of N_2O formed during SCR reaction.

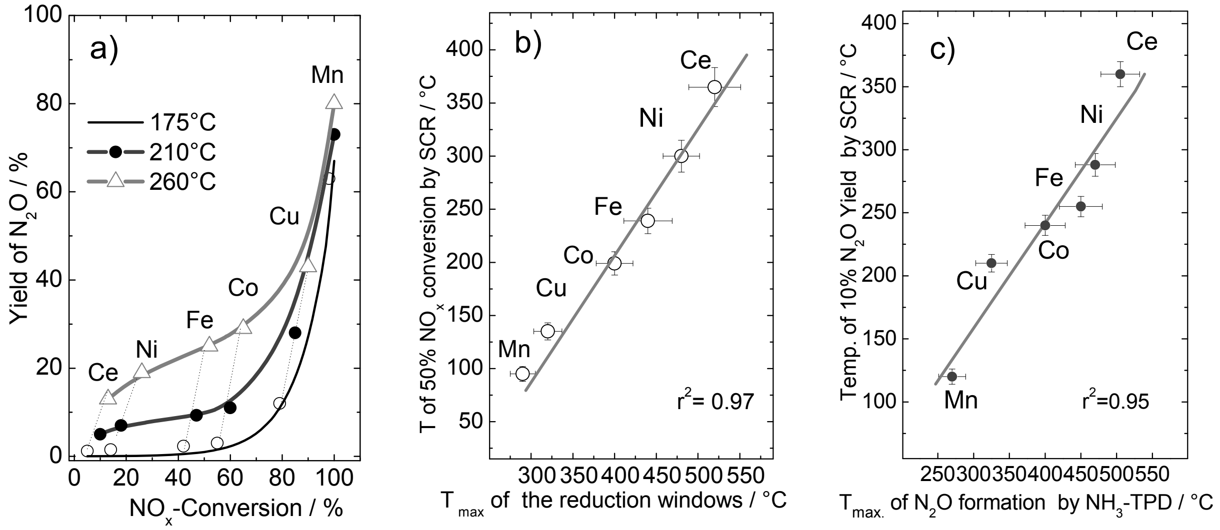

Fig. 1. NO_x-conversion and N_2O-yield over prepared catalysts during NH_3-SCR at 175, 210 and 260° (a) and correlation between the main reduction temperature of the catalysts during TPR with the temperature for 50 % of NO_x conversion and between temperature of N_2O formation by NH_3-TPD (b) and 10% N_2O yield (c) observed during NH_3-SCR (c) .

Conclusion

The obtained results illustrate the importance of quantitative and qualitative assessment of NO_x adsorption and catalytic oxidation of NH_3 over supported TMOs for the development of new SCR catalysts. A linear correlation between the reduction temperature determined by TPR and the temperature at which a NO_x-conversion of 50 % occurs over the catalysts during NH_3-SCR was observed (Fig.1b). This indicates that the reduction properties of the TMOs are the determining factors for the low-temperature activity during NH_3-SCR (Fig. 1c). Additionally, the adsorption of NO_x in the form of weakly bonded NO_x species and the oxidation activity of TMO containing catalyst are the key factors for the SCR reaction in the presence of ammonia and can be improved in a targeted manner.

Acknowledgments

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Research on the Shaping Process of PKR-2 Catalyst for a High-Temperature N_2O Decomposition With Using Capillary Rheometry

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Abstract* – *PKR-2 catalyst for N_2O abatement in HNO_3 plants is shaped by an extrusion process, from a mixture of catalyst powder and plasticizing additives. The catalyst mass composition, allowing for its trouble-free shaping on an industrial extruder and producing catalyst extrudates with the best mechanical parameters, was opimized using capillary rheometry.

Keywords – N_2O emission abatement, secondary catalyst, ammonia burner, rheological properties, PKR-2 catalyst mass, capillary rheometry, catalyst extrudates.

Introduction

New Chemical Syntheses Institute developed PKR-2 catalyst for a high-temperature N_2O decomposition. One of the important unit operations in the manufacturing technology of this catalyst is shaping by an extrusion. For a better control of catalyst production, it is necessary to assess the rheological properties of the mass, from which the catalyst extrudates are formed. The rheological properties describe the mass flow behaviour and constitute the material reaction to the shear stresses, leading to its deformation during the extrusion process. These properties depend on:

- mass composition, i.e. the type and amount of plasticizers, the content of batch water, grain size distribution of the catalyst powder,
- operating conditions of the extrusion process, i.e. temperature and extrusion velocity.

The rheological properties of PKR-2 catalyst mass were studied with using capillary rheometry. Formability and apparent viscosity of the examined mass samples were determined, depending on the mass composition and extrusion conditions.

The aim of the rheological studies was the optimization of PKR-2 catalyst mass composition in terms of producing the extrudates of a required mechanical strength and simultaneous ensuring a good mass formability. Te optimization involved the selection of batch water content, the type and amount of plasticizers. The Benbow-Bridgewater equation (Eg. 1) was used to indentify the main flow resistances of PKR-2 catalyst masses and to determine their rheological parameters [1]:

$$P_c = 2\ln\left(\frac{D_0}{D}\right)(\sigma_0 + \alpha V) + \frac{4L}{D}(\tau_0 + \beta V) \qquad (1)$$

where:

D_0 i D – barrel and capillary diameter,

L – capillary length,

V – extrussion velocity,

$(\sigma_0+\alpha V)$ – plasticity dependent on the extrusion velocity,

$(\tau_0 +\beta V)$ – shear stress, associated with a mass friction against the capillary wall.

Based on the extrusion pressure (P_c), measured at different extrusion conditions, the mass flow resistances, associated with the mass deformation at the capilary inlet $(\sigma_0+\alpha V)$ and mass friction against the capillary wall $(\tau_0 +\beta V)$, were determined.

Experimental

PKR-2 catalyst masses were prepared by mixing powdered catalyst precursor, batch water and plasticizers. Various plasticizers were tested, such as: inorganic acid, cellulose derivative, polyalcohol and polyglycol. The rheological properties of the catalytic masses were tested using the capillary rheometer CEAST SR20 Instron by measuring the total extrusion pressure and pressure in the capillary at different extrusion velocities and for two capillary lengths. Shaped masses were dried and calcined at a temperature of about 500°C, and then the mechanical strength of the extrudates was determined.

In the first stage, the optimal content of inorganic acid, organic plasticizers and batch water in PKR-2 catalyst mass was determined, allowing for trouble-free mass shaping in the continuous mode and producing extrudates of a required mechanical strength. The results shows, that the addition of inorganic acid in the amount of <1.5 wt.% (calculated on a dry mass weight) has a beneficial influence on the mechanical strength of the catalyst extrudates. The addition of organic plasticizer in the amount of 1 wt. % increases the plasticity of the mass, limits the liquid phase migration the during the extrusion process and increases the green strength of the shaped mass (extrudates). The content of batch water (≤ 35 wt.% calculated on the dry mass weight) was determined so as to obtain the mass of a good formability, without simultaneous lowering the mechanical strength of PKR-2 catalyst below the accepted level.

In the next step, the influence of various organic plasticizers addition on the rheological properties of the catalyst mass and mechanical strength of the final product, was investigated. The mass samples were prepared using the same amount of batch water and inorganic acid (determined in preliminary studies), while the amount of organic plasticizer/s was no greater than 1 wt. %. Based on the results of the rheological studies, carried out at different shear rates and for two capillary lengths, the parameters of the Benbow-Bridgewater equation, were calculated (Table 1).

Table 1

Benbow-Bridgewater parameters, calculated for PKR-2 catalyst mass with different combinations of plasticizers (M1 – cellulose derivative+inorganic acid, M2 – polyalcohol+ inorganic acid, M3 – polyglycol+inorganic acid, M4 - polyalcohol+cellulose derivative+inorganic acid) and mechanical strength of produced catalyst extrudates (W)

		PKR-2 catalyst mass			
		M1	M2	M3	M4
Benbow-Bridgewater parameters	σ_0	0.287	0.515	0.193	0.162
	α	$9{,}0\cdot10^6$	$6.0\cdot10^7$	$8.0\cdot10^6$	$3.4\cdot10^4$
	τ_0	0.014	0.295	0.009	0.026
	β	3.2	490.2	$1.2\cdot10^4$	1.1
	n	0.25	0.79	0.99	0.14
W [N/mm]		4.2	5.2	4.3	5.2

In the case of all studied PKR-2 catalyst masses, the greatest extrusion resistances generates the plastic mass deformation at the capillary inlet, whereas in the area of capillary mass flows easily ($\alpha>\beta$). The highest value of $(\sigma_0+\alpha V)$ was obtained for the mixture of polyalcohol and inorganic acid. On the other hand, the presence of these two plasticizers improves the mechanical strength of the catalyst extrudates. The lowest flow resistances at the capillary inlet were observed for the mass with the addition of polyglycol. However, in this case, the highest mass flow resistances in the capillary area were observed (mass friction against the capillary wall). This can be related to the mass dewatering during its formation in the capillary.

It was found, that after adding to the mass more than one organic plasticizer, the flow resistances, related both to the deformation of the mass at the capillary inlet and mass flow through the capillary, can be reduced. This synergistic plasticizers interaction was observed for the plasticizing additives mixture: polyalcohol+cellulose derivative+inorganic acid. The addition of this plasticizers mixture has a positive influence on the mass formability and rheological stability of PKR-2 catalyst mass (see Table 1, M4).

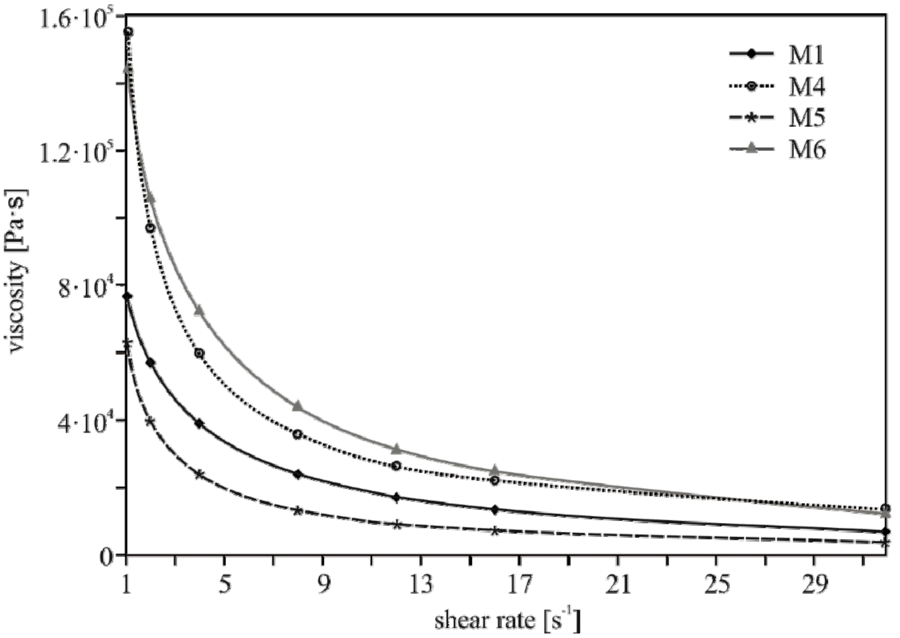

Fig. 1 Viscosity curves obtained for PKR-2 catalyst masses, containing different plasticizers mixtures (extrusion termperature = 56°C, capillary length = 10 mm): M1 (cellulose derivative + inorganic acid), M4 (polyalcohol + cellulose derivative + inorganic acid), M5 (polyglycol + cellulose derivative + inorganic acid), M6 (polyalcohol + polyglycol + cellulose derivative + inorganic acid).

In Figure 1, the viscosity curves, obtained for PKR-2 catalyst masses with the addition of various organic plasticizers mixtures, are shown. The results indicate, that regardless of the used plasticizing additives combination, the catalyst masses have complex rheological properties, clasyfying them as the pseudoplastic shear-thinning fluids. Various plasticizers have different influence on the mass flow properties and mechanical parameters of the catalyst extrudates. The addition of polyglycol in a mixture with another organic plasticizer (sample M5), increases the relative humidity of PKR-2 catalyst mass, significantly improves its formability and rheological stability. However, it leads to the production of catalyst extrudates with a lower mechanical strength (Table 2). The addition of polyalcohol (M4, Fig. 1), improves the mechanical strength of the catalyst extrudates (Table 2), but simultaneously deteriorates the mass formability, to the greater extent, the higher is its content in the catalyst mass. The reseaches show, that the mechanical properties of the catalyst can be improved, without significant deterioration of the mass formability, using a mixture of plasticizing additives: cellulose derivative + polyglycol + polyalcohol + inorganic acid+water. Polyglycol in mixtures with polialcohol plays a role of cross-linking agent, promoting the aggregation of polyalcohol macromolecules, surrounding the solid phase grains. This leads to an increase in the catalyst mass density and, as a consequence, to the increase of extrudates mechanical strength.

Table 2

Mechanical strength of catalyst extrudates (W), obtained from PKR-2 catalyst mass with different combinations of plasticizers: M1 (cellulose derivative+ inorganic acid), M4 (polyalcohol+cellulose derivative+inorganic acid), M5 (polyglycol+cellulose derivative+inorganic acid), M6 (polyalcohol+polyglycol+cellulose derivative+inorganic acid).

PKR-2 catalyst mass	W [N/mm]
M1	4.8
M4	5.2
M5	4.0
M6	6.4

Conclusion

Rheological studies of PKR-2 catalyst masses, with using capillary rheometry, showed, that they have complex rheological properties, clasyfying them as pseudoplastic shear-thinning fluids. Increasing the amount of batch water or polyglycol in the mass, improvess its formability, but has a negative influence on the mechanical strength of the catalyst extrudates. The mechanical properties of the catalyst can be improved by the additon of inorganic acid and polyalcohol. It was found, that mass flow resistances and mechanical strength of the final product, increase with the the molecular weight of organic plasticizer, contained in PKR-2 catalyst mass: polyglycol<cellulose derivative<polyalcohol. A positive synergistic effect of the addition of polyglycol and polyalcohol mixture was observed, consisting in improving the mass formability and its rheological stability, limiting a liquid phase migration and increasing the mechanical strength of the shaped catalyst. During the researches, the following optimal combination of the plasticizing additives was determined: polyalcohol+polyglycol+cellulose derivative+inorganic acid.

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The Influence of the Operating Conditions in Ammonia Burner on the Effectiveness of the Catalyst for a Nitrous Oxide Decomposition

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Abstract* – *The influence of the ammonia burner operating conditions on PKR-2 catalyst efficiency and structure was investigated. It was found, that the catalyst retains its initial activity even after 13 months of work at 890°C. Only its local overheating can lead to a decrease of its activity or deactivation.

Keywords – nitric acid plant, N_2O emission, greenhouse gas, N_2O abatement technology, catalytic performance, secondary catalyst.

Introduction

Nitrous oxide (N_2O) is a greenhouse gas, whose emission into the atmosphere is subject to increasingly stringent emission standards. One of the significant sources of this gas emission are the nitric acid plants. Nitrous oxide is formed as a by-product in the process of catalytic ammonia oxidation. It does not undergo any chemical transformations in the whole technological line of nitric acid manufacturing and is fully emitted into the atmosphere. Therefore, the use of an effective method of N_2O emission abatement is highly reguired [1]. One of such methods is the catalytic decomposition of nitrous oxide from a process gas stream at a high temperature. In this case, the layer of deN_2O catalyst is installed in an ammonia burner, directly beneath the catalytic gauzes [2].

The catalyst, which is to be used in ammonia burner, should have a high activity, selectivity and stability under the reaction conditions. A big chalange is to ensure a high mechanical strength and high abrassion resistance of the catalyst extrudates, as well as its long lifetime under the extremely difficult operating conditions (high temperature, possibility of local catalyst overheating, high water vapor pressure in the process gas stream).

New Chemical Syntheses Instiute has developed its own Fe_2O_3-Al_2O_3 catalyst (PKR-2), which is active in HT-deN_2O process. The catalyst works stably in many industrial installations and allows to reduce N_2O emission to the desired level. Nevertheless, the investigations on the improvement of the catalyst functional properties are still carried out. They are focused on two practical aspects: modification of the catalyst manufacturing technology and determination of the influence of ammonia burner operating conditions.

The studies, described below are related to the determination of the catalyst resistance to the deactivation (thermal and time-related).

Experimental

The catalyst activity was tested in a pilot ammonia oxidation plant in the flow of a real nitrous gases mixture. Parallel to the studies of PKR-2 catalyst activity and selectivity, the changes in its structure were also investigated. In the adopted research metodology, the activity of the catalyst samples with different "thermal history" was compared with the fresh catalyst sample (reference sample).

All measurements were performed under the identical operating conditions: p=5 bar, T=890°C, $V_{mix,inlet}$=56 Nm^3/h. The run time of the test in the pilot plant was 120 h. During the measurements, the same volume of deN_2O catalyst bed was used, as well as the same catalytic gauzes package. The diameter of ammonia burner was 100 mm. The catalyst activity was determined on the basis of the difference of N_2O concentration in nitrous gases stream, measured downstream of Pt-Rh catalytic gauzes and after a secondary catalyst layer, at the outlet of the reactor. For the activity tests, the following PKR-2 catalyst samples were selected: P1 – fresh (reference) catalyst calcined at a temperature of 500°C, P2 – catalyst after 100 days of work in an industrial installation, 3 – catalyst after 400 days of work in an industrial installation, 4 – catalyst overheated at a temperature of 1100°C, 5 – catalyst overheated at a temperature of 1400°C.

In Fig. 1, the activity of tested PKR-2 catalyst samples was compared with the reference sample activity.

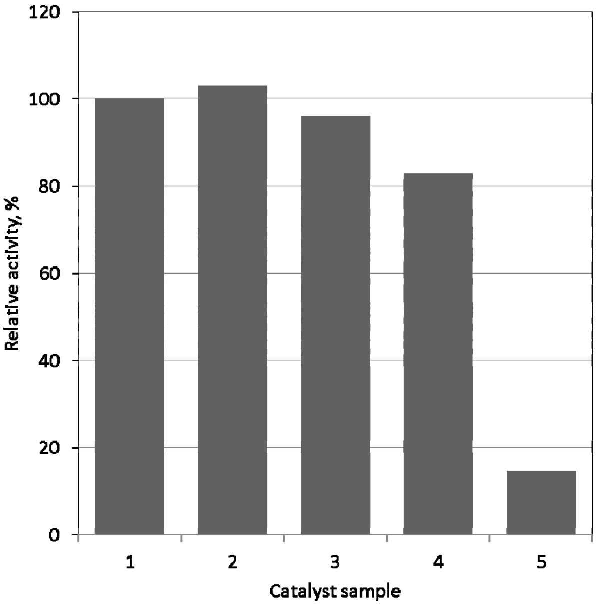

Fig.1. The comparison of PKR-2 catalyst samples activity, tested in a pilot plant.

The PKR-2 catalyst after shaping and calcination at a temperature of 500°C (P0) is a mesoporous material with an average pore diameter of 20 nm and specific surface area of 50 m^2/g. In case of the catalyst, subjected to a high temperature of 890°C (P1), the sintering process is observed. In the catalyst structure disappear the mesopores and increases the average pore diameter, while a total pore volume does not change.

Table 1.

The basic physicochemical parameters of PKR-2 catalyst samples, tested in a pilot plant

Sample	S, m^2/g	V, g/cm^3	$V_{mesop.}$, g/cm^3	d_{pore}, nm	P, %	Comments
P0	50	0.27	0.26	22	53	The fresh sample
P1	9	0.27	0.01	115	56	Sample P0 after test in the pilot plant
P2	2.2	0.19	0.00	350	49	After work in the industrial plant (100 days)
P3	1.8	0.22	0.00	490	51	After work in the industrial plant (400 days)
P4	2.1	0.16	0.00	216	44	Overheated at 1100°C
P5	<0.1	<0.01	-	-	<4	Overheated at 1400°C

where: S - surface area, V – total pore volume, $V_{mesop.}$ – volume of mesopores, d_{pore} – average pore diameter , P- porosity.

Moreover, a thermal shrinkage of the catalyst extrudates, 6-percent weight loss of the catalyst bed and lowering of a specific surface area is observed. Longer operation of the catalyst in ammonia burner does not cause any futher changes in its structure (samples P2 and P3).

Exposure of the extrudates to a temperature higher than the operating temperature in ammonia burner (1100ºC (P4) and 1400ºC (P5), e.g. due to the local catalyst overheating, causes further changes in the catalyst structure, due to the greater progress of sintering process. In Table 1, the physicochemical parameters for different PKR-2 catalyst samples are given.

Conclusion

The significant changes in the PKR-2 catalyst structure are observed in the initial period of its operation in the ammonia burner. The sintering of the catalyst extrudates causes the decrease of catalyst specific surface area, as well as disappearance of mesopores and appearance of macropores in its structure. Calcination of the catalyst at a temperature of 500ºC does not allow for the complete stabilization of its structure. Exposure of the catalyst to a higher temperature results in a weight loss of the catalyst bed and leads to a reduction of the catalyst bed volume.

During the catalyst work, its gradual sintering is observed, accompanied by an increase in the pore diameter. Despite the changes in the catalyst structure, its operation at a temperature of 890ºC in the ammonia burner does not cause any negative changes in its activity. The catalyst retains its initial activity, even after 13 months of work in the industrial plant.

Overheating of the catalyst (1100°C) causes further sintering of the extrudates. At a higher temperature, the porosity and a total pore volume of the catalyst are decreased, but despite this, only a slight lowering of its activity is observed. Its significant overheating above this temperature (1400°C) causes the complete destruction of the catalyst structure and leads to its permanent deactivation.

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Application of UV, H_2O_2 , H_2O_2/UV, Fe(II)/H_2O_2 and Fe(II)/H_2O_2/UV Process for Oxidation of Organic Compounds in Printed Circuit Boards Wastewater

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Abstract – The paper deals with possible use of acidification and* UV, H_2O_2 , H_2O_2/UV, Fe(II)/H_2O_2 and Fe(II)/H_2O_2/UV *(Fenton and Photo-Fenton) process for purifying contaminated printed circuit boards wastewater (pH=10.5, Chemical Oxygen Demand, COD=5 980 mg O_2/L, Total Organic Carbon, TOC=2 100 mg/L). Application of acidification and Photo-Fenton process was allowed to decrease COD (98.5%) and TOC (98.1%) in treated wastewater.

Keywords – Advanced Oxidation Processes, Fenton, Photo-Fenton, Free radicals, Printed circuit boards wastewater, Organic compounds

Introduction

The production of Printed Circuit Boards (PCBs), is associated with the generation of a significant amount of wastewater containing organic compounds and heavy metals (i.a. Cu, Sn, Ni) [1-2]. The source of alkaline wastewater are photochemical processes in which alkaline solutions (i.a. Na_2CO_3, K_2CO_3, NaOH) with the addition of anti-foaming agents are used [3-4]. The COD value of alkaline wastewater may be up to even 15 000 mg O_2/L [3]. The treatment of these wastewater involves acidification (HCl or H_2SO_4) to precipitate insoluble polymers at pH<5. In addition, activated carbon is used and the effectiveness (COD reduction) of this method depends on many factors. The COD values in treated wastewater reported in literature (400 mg O_2/L) are usually not achieved [5]. Therefore, in order to increase the reduction of COD, AOPs were applied.

Materials and methods

Wastewater from the printed circuit board production plant was used in the study. The studies were carried out in a coagulator (500 mL) and UV photoreactor (580 mL, 11 W, Osram® Puritec HNS). In the first stage (determination of the dependence of COD change on the pH of wastewater) for the acidification of wastewater concentrated H_2SO_4 was used. In the second stage, the wastewater after acidification and sludge filtering was subjected to UV treatment (11 W, 0-60 min), H_2O_2 (3 g/L, 0-60 min), H_2O_2/UV (3 g/L, 11 W, 0-60 min), Fe(II)/ H_2O_2 (pH=2.25, Fe(II)/H_2O_2=0.17, H_2O_2 5 g/L, 0-60 min) and Fe(II)/H_2O_2/UV (11 W, pH=2.25, Fe(II)/H_2O_2=0.17, H_2O_2 5 g/L, 0-60 min). During the process, samples of wastewater were taken, alkalized (NaOH) to pH=9 and filtered by using syringe filter (0.45 µm). The remaining of H_2O_2 was removed by using catalase before the COD determination. After that the pH (EN ISO 10523:2012), COD (ISO 15705:2005) and TOC (EN 1484: 1999) were determined.

Results

Wastewater used in the study was characterised by alkaline reaction (pH=10.5) and high COD and TOC values (COD=5 980±900 mg O_2/L, TOC=2 100±315 mg/L), which was an indication of a high content of organic compounds. In the Fig. 1 the dependence of COD and TOC on the pH of wastewater is presented. The lowest COD and TOC values were noted at pH 1-5 (790-840 mg O_2/L and 315-390 mg/L respectively). Wastewater after acidification and filtering of separated sediments was characterized by low susceptibility to UV and H_2O_2, and changes of COD and TOC values of wastewater were small, as shown in the Fig. 2. Increased effectivity was achieved by using the UV/H_2O_2 process. In this case, the lowest COD and TOC values (in the range of 360-365 mg O_2/L and 250-255 mg/L respectively) were obtained after 50 and 60 minutes of the process. The highest effectiveness was achieved in the Fenton and Photo-Fenton process.

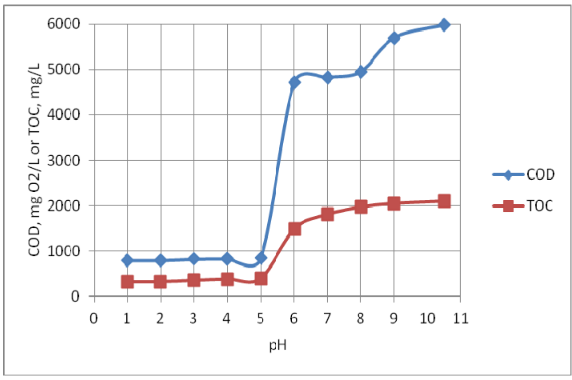

Fig.1. The changes of COD and TOC after acidification with H_2SO_4

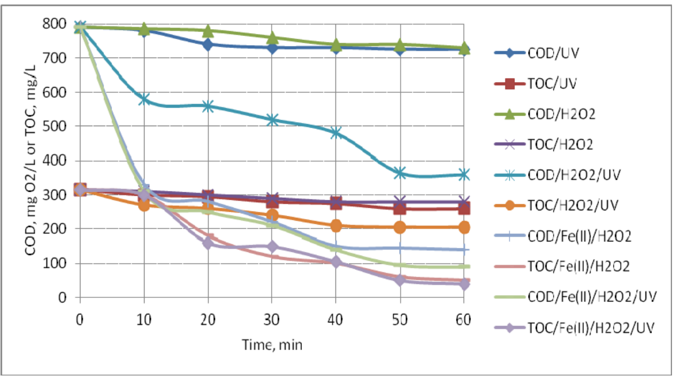

Fig.2. The changes of COD and TOC after an additional application of oxidation processes

In these cases, the lowest COD and TOC values were also obtained after 50 and 60 minutes of the process. For the Fenton process, COD values were reduced from 790 to 140 mg O_2/L and for TOC from 315 to 50 mg/L. For the Photo-Fenton process, COD values were reduced to 90 mg O_2/L and TOC values even to 40 mg/L. In the first stage (acidification only) the effectiveness of removal of COD and TOC reached 86.8% and 85.0%, respectively, and in the case of combining both methods (acidification and Photo-Fenton process), 98.5% and 98.1%, respectively.

Conclusion

The wastewater acidification method (by using concentrated H_2SO_4) applied as a pre-treatment method allowed to remove a significant amount of organic compounds from the tested wastewater as a result of precipitation of polymers which were insoluble in an acidic environment. Pollutants remaining in wastewater were not susceptible to UV and H_2O_2. The highest treatment efficiency was achieved with AOPs (H_2O_2/UV, Fe(II)/H_2O_2, Fe(II)/ H_2O_2/UV) as a result of oxidative action of hydroxyl radicals (•OH).

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Removal of Volatile Organic Compounds (VOCs) on Synthesized Zeolites

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***Abstract* – The aim of this study was synthesis of Y-zeolite by recrystallization of natural clay materials, its application to adsorption of selected carbonyl compounds and modelling the adsorption equilibria and dynamics. High adsorption capacity and the possibility of using synthesized zeolite as a filling of zeolite rotors were demonstrated.**

Keywords – synthetic zeolites, volatile organic compounds, acetone, methyl ethyl ketone, adsorption

Introduction

Volatile Organic Compounds (VOCs) are substances, which presence in the environment contributes to formation of ozone, which in turn favors the formation of photochemical smog and secondary pollutants in the form of organic aerosols. Sources of VOC emissions to the atmosphere are primarily emissions of fumes, evaporation of fuels and solvents, and biomass combustion [1]. The commonly used method of VOC emission reduction is adsorption on active carbon. However, due to the hygroscopicity and flammability of coal, alternative adsorbents are sought. Among which we can distinguish synthetic zeolites, which are characterized by high adsorption capacity and thermostability, which enables thermal regeneration at temperatures above 200°C and their multiple use.

Zeolite synthesis

Zeolite was prepared by indirect synthesis including recrystallization of natural clay material. The synthesis process consisted of three stages, activation of the clay material, as well as ageing and crystallization of the reaction mixture. Three clay materials, kaolinite, bentonite and halloysite were selected for the study. The influence of clay material type, temperature and time of subsequent stages of synthesis on the process efficiency was investigated. The selected synthesis product was subjected to instrumental analysis.

VOC adsorption

Adsorption of acetone, MEK (methyl ethyl ketone) and acetone/MEK mixture in a specially prepared installation was carried out. The values of equilibrium concentration in the constant phase (q_e) were calculated using the numerical integration method. It was shown that the Y-type zeolite obtained had at least comparable adsorption capacity to carbonyl compounds in comparison with commercially used adsorbents (zeolite X13, active carbon).

Modelling the adsorption equilibrium

Isotherms of acetone and MEK adsorption on Y-zeolite were determined and then the process dynamics was calculated. The approximation accuracy of experimental and model value of the maximum adsorption capacity (q_m) was chosen to evaluate the quality of model matching. Its adoption as a selection criterion enabled to indicate Langmuir and Langmuir-Freundlich models as the most adequate to the mathematical description of adsorption equilibrium.

Simulation of the concentration profiles distribution

The parameters K, q_m and n, determined during modelling of equilibrium, were used to simulate the distribution of concentrations in the adsorption column filled with zeolite. The Equilibrium-Dispersion model (R-D) was used to model the adsorption dynamics of single component systems:

$$\left[\left(1+\left(\frac{1-\varepsilon_t}{\varepsilon_t}\cdot\rho_s\right)\cdot\left(\frac{\partial q_i}{\partial C_i}\right)\right)\frac{\partial C_i}{\partial t}\right]+\left(\frac{u}{\varepsilon_t}\right)\cdot\left(\frac{\partial C_i}{\partial l}\right)=D_a\frac{\partial^2 C_i}{\partial l^2} \qquad (1)$$

The following Danckwert's boundary conditions were maintained:

for $t > 0$; $l = 0$:

$$u\cdot\left[C_{0,i}(t)-C_i(t,0)\right]=-\varepsilon_t\cdot D_a\cdot\frac{\partial C_i(t,0)}{\partial l} \qquad (2)$$

for $t > 0$; $l = L$:

$$\frac{\partial C_i(t,L)}{\partial l}=0 \qquad (3)$$

where: C_i and q_i – concentration in the mobile phase [mmol/cm^3] and on the adsorbent surface [mmol/g], t – duration of the process [s], l – distance counted from the beginning of column [cm], D_a – effective dispersion coefficient [cm^2/s], ε_t – total porosity [-], ρ_s – specific density of adsorbent grain [g/cm^3], u – velocity counted per empty cross-section of column [cm/s], L – column length [cm], $C_{0,i}$ – inlet concentration of i component [g/cm^3].

As a result of supplementing R-D model with Langmuir-Freundlich equation and estimation of the heterogeneity parameter n, the exact coverage of experimental points in single-component systems was obtained (Fig. 1A). For the two-component system (acetone, MEK) calculations were performed using two models, R-D or Kinetic-Dispersion (K-D), supplemented with the extended Langmuir equation. The calculations showed a need to search for values of all parameters (k, K and q_m) (Fig. 1B).

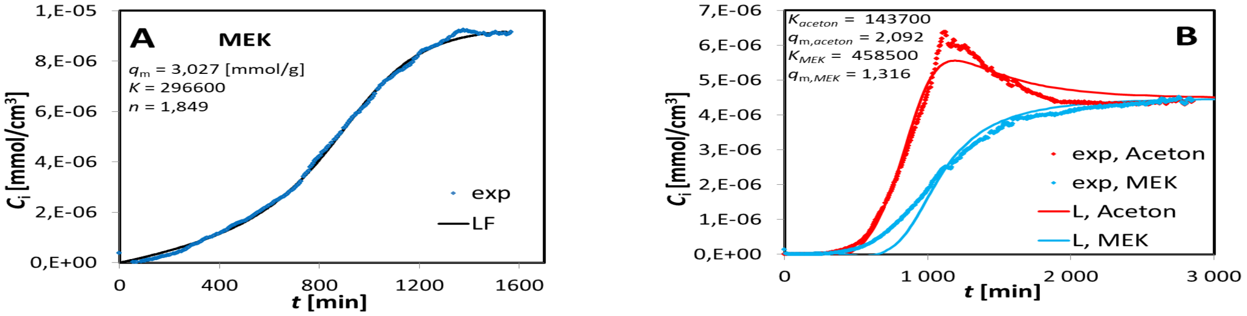

Fig. 1. Modelling of concentration profiles (A) of MEK and (B) acetone/MEK mixture in the column filled with synthesized zeolite. Simulation with R-D model.

Acknowledgments

The adsorption analysis was performed at OTTO Engineering Polska Sp. z o.o.

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N,N-Dibutyl Lauramide as New Alternative Plasticizer for Polyvinyl Chloride

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Abstract* – *In this study, N,N-dibutyl lauramide (DBLA) has been synthesized and tested as new plasticizer for polyvinyl chloride (PVC), alternative to common toxic phthalate esters. It has been found that DBLA has excellent compatibility with PVC and efficiently reduces its glass transition temperature from 83,5 to -7,7 ºC at plasticizer content 30 wt%.

Keywords – polyvinyl chloride, plasticizer, fatty acid dibutylamide, glass transition, thermal stability

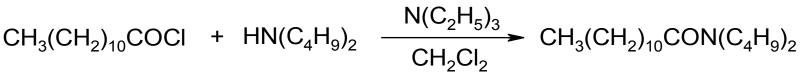
Introduction

Until recently, phthalate esters were most commonly used plasticizers for polyvinyl chloride (PVC). However, phtalates have been identified as reproductive and developmental toxicants, as well as probable human carcinogens [1]. Thus, the development of new phthalate-free PVC plasticizers is of great demand. Fatty acid dialkylamides have been reported as efficient primary PVC plasticizers which can be prepared from vegetable oils or their derivatives [2]. Further research, however, showed reduced heat resistance of plasticized PVC compositions based on unsaturated fatty dialkylamides.

The aim of this study was to evaluate plasticizing efficiency, as well as migration resistance of new saturated fatty acid dibutylamide, namely N,N-dibutyl lauramide.

Experimental section

N,N-dibutyl lauramide (DBLA) was synthesized according to following scheme.



$$CH_3(CH_2)_{10}COCl + HN(C_4H_9)_2 \xrightarrow[CH_2Cl_2]{N(C_2H_5)_3} CH_3(CH_2)_{10}CON(C_4H_9)_2$$

Polyvinyl chloride Ongrovil® S5258 (BorsodChem, Hungary) was used for the preparation of plasticized compositions. PVC/DBLA composites containing 20 and 30 wt% of plasticizer were prepared by solvent-cast film method using dichloroethane as a solvent.

The tensile tests were carried out using a universal tensile test machine P-50 (Milaform) at a deformation rate of 10 mm/min. According to mechanical testing data, PVC/DBLA films have lowered tensile strength, as well as significantly higher elongation at break, compared to neat PVC (Table 1). The last parameter indicates an improved flexibility imparted by plasticizer.

Table 1

Mechanical properties of PVC/DBLA films

Sample	Tensile strength, MPa	Elongation at break, %
PVC control	37,5 ± 1,5	16,5 ± 3,5
PVC/20% DBLA	17,8 ± 3,5	191,6 ± 4,5
PVC/30% DBLA	12,8 ± 2,0	211,5 ± 5,5

Thermal gravimetric analysis (TGA) was performed using a TGA Q500 (TA Instruments). About 10 mg of each sample was heated from 30 °C to 700 °C with a heating rate of 10 °C/min under an air atmosphere. According to the TGA data, PVC/DBLA composite has a thermal decomposition point (which was defined as the temperature of 5% weight loss ($T_{\Delta m=5\%}$)) at 221 ^{o}C that is very close to that for neat PVC (Table 2).

Table 2

TGA data for plasticized PVC composition

Sample	$T_{\Delta m}$=5%, °C	$T_{\Delta m}$=10%, °C	$T_{\Delta m}$=20%, °C	$T_{\Delta m}$=50%, °C
PVC control	226	257	277	301
DBLA	182	203	228	268
PVC/30% DBLA	221	227	235	265

Plasticizing effect of DBLA on PVC was studied using DSC Q2000 TA Instrument analyzer. The heating process was performed from -90 to 150^{o}C at 20 ^{o}C/min. Glass transition curves obtained for PVC/DBLA compositions are illustrated in Fig. 1. The neat PVC had glass transition temperature T_g of 83,5 ^{o}C. T_g decreased significantly on addition of DBLA plasticizer, reaching the value -7,7 ^{o}C for PVC/DBLA (30%).

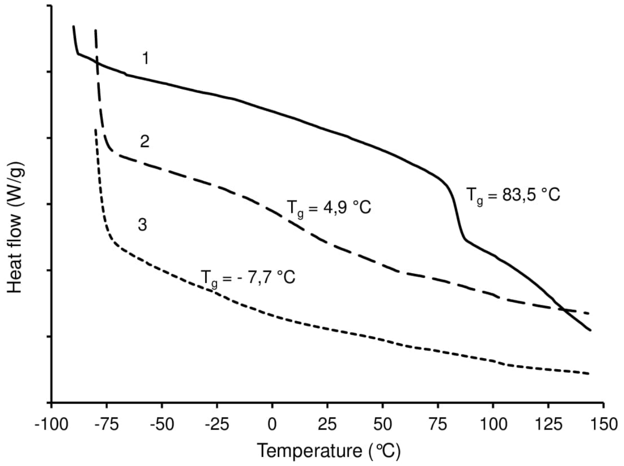


Fig.1. Glass transition curves: 1 - PVC, 2 - PVC/DBLA (20%), 3 - PVC/DBLA (30%)

For evaluation the resistance of plasticizer to migration, PVC/DBLA films of 80 x 80 mm size were placed between two lists of filter paper. The sandwiched materials were kept in contact by placing them between glass plates. The migration of plasticizer was studied at 25 ^{o}C over 21 days period. The amount of plasticizer that migrated from PVC film was found to be 1,5% from its total content.

Conclusion

Thus, it can be concluded that N,N-dibutylamide of lauric acid (DBLA) is an efficient, primary plasticizer for PVC resin. The plasticizing efficiency of DBLA is very close to that of common phthalate esters. Moreover, PVC/DBLA compositions showed excellent thermal stability, as well as high migration resistance of plasticizer from polymer matrix.

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Method of Alkaline Destruction as the Way to Stop Methanogenic Effluent's Gasification

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Abstract* – *We propose using a method of alkaline destruction to solve the problem of effluent's gasification. It can provide production synthesis gas and humate.

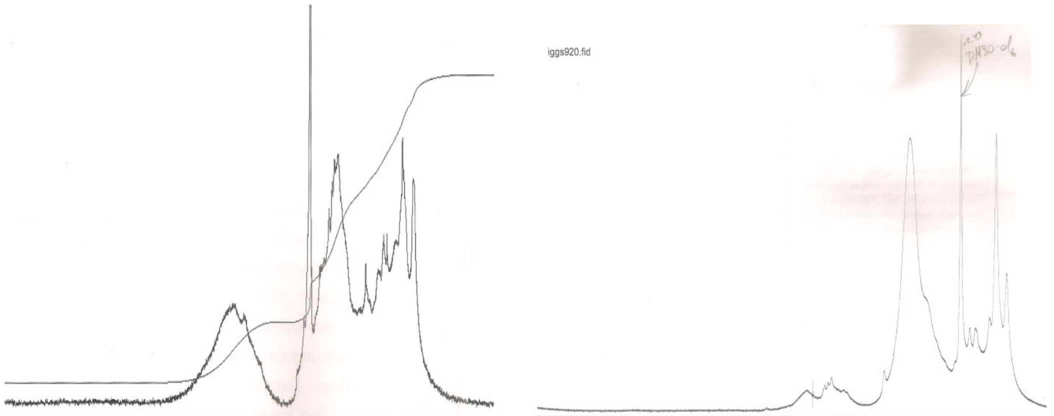
Keywords – alkaline destructions, humate, fertilizer gasification, NMR spectroscopy, effluent.

Introduction

One of the main problems which limit the distribution of biogas plants is the fertilizer gasification [1]. This process provides a problem of the fertilizer storage. Previously additional fermentation was conducted to solve this problem. It is characterized by additional biogas output, but it suppose to build additional biogas reactor and this it still does not supply completed fermentation [2]. We propose the process of alkaline destructions to solve this problem. It can provide production synthesis gas and humate.

The cylindrical stainless steel reactor with a volume of 4 l was used to the research of chicken manure alkaline destruction. The process was carried out at a temperature of 200 °C during 3 h. Reactions mixture consists of 1 kg dried effluent 0,3 kg effluents liquid phase 0,3 kg potassium hydroxide. The effluent was obtained by anaerobic digestion with HRT time of 10 days in thermophilic condition (50 °C) [1] and after that was detached from the liquid phase. The method of one-dimensional NMR spectroscopy on 1H 31P nuclei was used foraffiliation of obtained product to humates and determine their quantit Samples of produced compounds were prepared using the standard method of NMR-spectroscopy sample preparation (GOST R 8.620-2006). The quantity of free humic acids was analyzed by method sedimentation using concentrated hydrochloric acid (GOST R 54221-2010).

The obtained product was characterized by absent microbiological activity which is related to the aim of work. NMR spectra of obtained product were appropriate to the peak of NMR spectra of natural humic acids of fertile soil (fig.).



a) b)

Fig.1 NMR-spectra of humic acids a) of natural humic acids of fertile soil b) of sample produced under alkalinity destruction of chicken manure

The content of free humic acids was 1,01% of dry matter. This content corresponds to optimal humates concentration in the fertilizers which are in the range of 1 to 2% [3]. It means that achieved fertilizer is more attractive to achieve better quality and quantity of plant.

Conclusion

Therefore, the method of alkaline destruction is assembled to solve the problem of effluent excess gasification of methanogenic effluent's. In addition, this approach can increase the economic attractiveness of anaerobic digestion due to the simplicity of the proposed installation and obtaining of humates.

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Mass Transport of Micro- and Macro-Molecule Compounds of Phosphorous Base Fertilizer Fortified with Protein in Soil Matrix

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Abstract - Microgranule phosphorous soil fertilizer based on a post-production waste was developed. Diffusion of micromolecule components of the granule in soil matrixes was measured. Degradation and diffusion of protein components in soilmatrix was determined.

Keywords - Phosphorous fertilizers, fertilizers fortified with protein, protein diffusion in soil, mass transport, protein degradation in soil,

Introduction

In recent years there has been a significant increase in the prices of phosphorous fertilizers, which made it necessary to seek alternative, more cost-effective solutions in the field of plant fertilization. Much cheaper fertilizers containing partially decomposed phosphorite, have become an alternative to the existing phosphorus sources, such as superphosphate [1-2].

Raw material for the production of such fertilizers can also be obtained from animal bones containing natural hydroxyapatite. Therefore, we developed a mineral phosphate fertilizer based on ash obtained by incinerating the meat industry wastes. The fertilizer in the form of a microgranule was supplemented with additives sourced from natural raw materials, i.e., protein preparations based on post-production waste (milk serum, soy paste, eggs).

In this project we measured the mass transport of the microgranule components in two different model solid matrixes composed of sand and standardized soil. The mechanism of protein decomposition during the fertilization process was proposed.

Methods

Microgranules were prepared using a laboratory pan granulator. The granule was composed of incinerated and grounded bones, lake chalk and protein isolates from milk serum, soy and chicken egg proteins. A microgranule (0.5 g mass) was placed on the bottom of a 15-ML cylinder with piston and a matric scale on the side-wall. Seven identical cylinders were used for the experiments. The cylinders were filled with wet sand or wet standardized soil (both with a predefined moisture content) with the height of 4.5 cm. The samples of the solid matrixes (sand and soil) were withdrawn at different time intervals; 5 mL slices of matrixes were acquired at different distances from the microgranule (from the bottom of the cylinder). Next, the samples were mixed with 5 mL of 0.1 M NaCl solution and vortex-homogenized. The supernatants obtained were subjected to HPLC, HPLC-SEC and Lowry method analyses, to determine the mass transport of ions and proteins through the matrix.

Results and discussion

Typical results of the concentration analysis of a protein from milk serum isolate and micromolecule components of microgranules in the matrix samples that were acquired at different distances from microgranule and different time intervals are presented in Fig.1 and

Table 1. It can be observed that the maximum of the protein concentration is reached after 48 h at the distance of 1.5 cm from the microgranule. The concentration of the protein drops rapidly with increasing the distance, and practically vanishes at 4.5 cm away from the microgranule. Moreover, the concentration of the protein decreases in time, which is caused by its degradation. The latter is confirmed by increasing ammonia ion concentration with increase in time (Table 1). The concentration of other ions reaches quickly its maximum due to fast diffusivity of small ions in the solid matrix. The results obtained for other protein isolates were similar to those reported above.

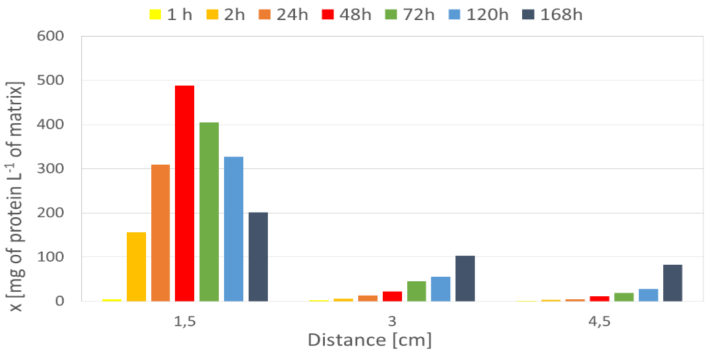

Fig.1. Protein concentration at different distances from microgranule containing milk serum isolate.

Table 1

Concentration of ions at the distance of 1.5 cm away from the microgranule measured at different time intervals.

Time	ammonium	potassium	magnesium	calcium	nitrate	phosphate	sulphate
[h]	μg of ion mL^{-1} of matrix						
6	0.376	52.05	6.27	29.96	1.67	1.19	374
24	0.360	66.02	9.62	16.35	1.22	8.61	303
48	1.96	59.97	7.84	22.83	0.68	3.36	278
72	3.59	57.10	8.96	20.58	0.79	3.18	296
120	33.5	58.56	8.09	27.93	0.62	2.67	321
168	34.1	55.27	11.33	36.16	1.58	3.02	449

Conclusion

The macromolecule components of the microgranule fertilizer diffuse through the solid matrix very slowly. The transport of the proteins is accompanied with their degradation, which induces formation of ammonium ions. The maximum of the protein concentration and ammonia ions is reached at very close distance from the microgranule, therefore, the fertilizer granule should be placed in vicinity to the plant grain.

Acknowledgments

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Using the Modern Software for Life Cycle Assessment in the Preparation of an Engineer in Automation and Computer-Integrated Technologies

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Abstract* – *A new course «Engineering for Sustainable Development» is introduced for bachelors of specialization «Computer-Integrated Technologies of Sustainable Chemical Productions» by the Department of Cybernetics of CTP. One-third of the discipline is addressed life cycle assessment issue, the practical part of which is implemented through the use of SimaPro software.

Keywords – automation and computer-integrated technologies, bachelor study, engineer, life cycle assessment, SimaPro, sustainability

Introduction

The Department of Cybernetics of Chemical Technology Processes of the National Technical University of Ukraine «Igor Sikorsky Kyiv Polytechnic Institute» prepares specialists in the direction of «Automation and Computer-Integrated Technologies» (specialization «Computer-Integrated Technologies of Sustainable Chemical Productions»). Gaining knowledge and creating skills that can be implemented in the field of environmental safety, green growth, and low carbon development by future engineers in the automation of sustainable chemical productions requires the introduction of new educational developments.

«Engineering for Sustainable Development» course for ACIT bachelors

Educating students of engineering direction in sustainability is very important as for future challenges' solvers [1]. Igor Sikorsky KPI actively implements principles and approaches of education for sustainable development within the framework of the target integrated program "Sustainable Development". In particular, it is a scientific and professional master degree programs with specializations in sustainability, university-wide disciplines on sustainable development («Sustainable Innovative Development», «Basics of Engineering and Technology for Sustainable Development», «Inclusive Green Growth», and «Foundations of Sustainable Development», last one is delivered in English), programs for the professional qualification improvement of scientific and pedagogical staff of universities, etc.

So, among others, 4.5 credits course «Engineering of Sustainable Development» was started for bachelors of the third year of study of the specialization «Computer-Integrated Technologies of Sustainable Chemical Productions» a few years ago. This discipline joins the issues of green chemistry, resource-efficient and cleaner production, and life cycle assessment of product systems. Reading requires professors to continually update and refine materials of the course, use of active forms of learning. The last component of the course introduces students to principles of circular economy, life cycle thinking and its implementation through the creation of life cycle management system on production, but first of all, with the role of life cycle assessment in the development of green economy.

Life Cycle Assessment topic and SimaPro software

Life cycle assessment of product systems is presented taking into account relevant editions of international environmental standards ISO (subfamily 1404X). When considering this topic, students are acquainted with key concepts and methods of life cycle assessment, phases and stages of the procedure, and peculiarities of working with databases.

Part of workshops of the course «Engineering of Sustainable Development», in particular on the topic of life cycle assessment, is performed in SimaPro version 9.0. This PRé Sustainability software is a leader among life cycle assessment applications and allows to transparently model and analyze life cycle of product systems, evaluate the environmental impact of a product at all stages of life cycle, identify hot spots in each link of a supply chain. The SimaPro software distinguishes among other life cycle assessment packages by

- the graphical representation of the product life cycle model,
- review of substances unconsidered in assessment and the data of all projects created,
- setting up user-defined parameters for calculations and waste scenarios [2].

SimaPro uses more than ten inventory databases in the calculations, including ELCD of the Joint Research Center of the European Commission and the ecoinvent LCI of the ecoinvent Association, and nearly thirty methods for life cycle assessment on the user's choice, among which such commonly used as Ecological scarcity, ReCiPe, and ILCD.

The use of SimaPro software for performing by students a number of analytical and accounting tasks in the cycle of computer workshops allows them to

- acquire skills to assess and analyze the impact of environmental aspects of the product,
- offer improvements of product system on the basis of life cycle assessment,
- gain experience in identifying the aspects of products characterized by low environmental sustainability, in using life cycle thinking for the development of new and improvement of existing products.

The practical part of the «Life Cycle Assessment» component has been developed in line with recommendations of the software's developers [3] and up-to-date works of leading scientists, researchers and practitioners in life cycle assessment, e.g. [4].

Conclusion

The life cycle thinking implemented through life cycle management methods and instruments is one of the keystones for engineering education in sustainability. Understanding the role of eco-design and provision of practical skills in life cycle assessment are powerful drivers of change for the chemical industry and beyond.

Acknowledgments

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Disinfection of Sewage from Municipal Wastewater Treatment Plants of Lviv

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Abstract* – *Devoted to the problem of sewage treatment by ultraviolet radiation. This method can clear the water from microbiological contamination and thereby improve water quality.

Keywords – water treatment, disinfection, UV-radiation, microflora, sewage.

Introduction

The reservoirs contain a large number of microorganisms: clean reservoirs – tens and hundreds of thousands of microorganisms in 1 m^3, contaminated – millions and billions of microorganisms in 1 m^3. Their number depends on the season (in summer, the number of microscopic algae and cyanobacteria, which can cause water blooms, is very high in reservoirs). Among them there are species that constantly inhabit the reservoirs, as well as those that fall there with sediments, sewage, and so on. Microflora is represented by various groups of microorganisms – bacteria, microscopic mushrooms, actinomycetes, algae, protozoa are found [1].

The most simple, cheap and widely used method of decontaminating water is chlorination. In Ukraine chlorination of water began to be used since 1908. The degree of decontamination depends mainly on the concentration of active chlorine, contact time, pH value and water temperature. The main disinfectant is active chlorine. However, despite the effectiveness of pathogenic bacteria, chlorination does not provide epidemic safety for viruses. Also, the negative property of such a method is the formation of organochlorine compounds and chloramines. [2].

One of the alternatives to chlorination of water is the decontamination of ozone. Ozone is a universal reagent, because it can be used for decontamination, discoloration, deodorization of water, for removal of iron and manganese. This method also has its disadvantages: by-products of ozonation – aldehydes (formaldehyde) and ketones, as well as the complexity and high cost of ozone production and the need for constant monitoring of ozone production [3].

Main part

One of the most effective methods of disinfecting water is ultraviolet irradiation. The effect of UV radiation on different types of microorganisms has the same nature, the main mechanism of which is the destruction of DNA and RNA structures in microorganisms under the influence of radiation in the region of 220-280 nm, the maximum bactericidal action takes place at a wavelength of 260 nm [4].

Ultraviolet radiation is instantaneous, at the same time, the radiation does not add water to the residual bactericidal properties, as well as the smell and taste. Water treatment with UV radiation does not lead to the formation of harmful by-products of chemical compounds [5].

The efficiency of sewage treatment from bacterial contamination by UV-radiation was studied for municipal sewage treatment plant № 2 of Lviv.

The sanitary-epidemiological assessment of the quality of water was determined by the indicator of the total microbial number (TMN) – the total number of bacteria in 1 cm^3 of the water being studied. TMN estimates the total contamination of sewage by microorganisms [6]. The essence of the method is to determine the total number of microorganisms that can grow on meat-peptide agar with temperature of 37 ± 0.5 ℃ for 24 ± 2 hours per 1 cm^3 of water, followed by the account of the colonies grown in this medium.

Experiments were carried out at different time (from 5 s to 20 s) and for different thickness of the layer of the investigated liquid (from 25 mm to 45 mm).

To study the influence of ultraviolet light on the decontamination of microorganisms, a UV installation of the tray type, shown in Fig. 1

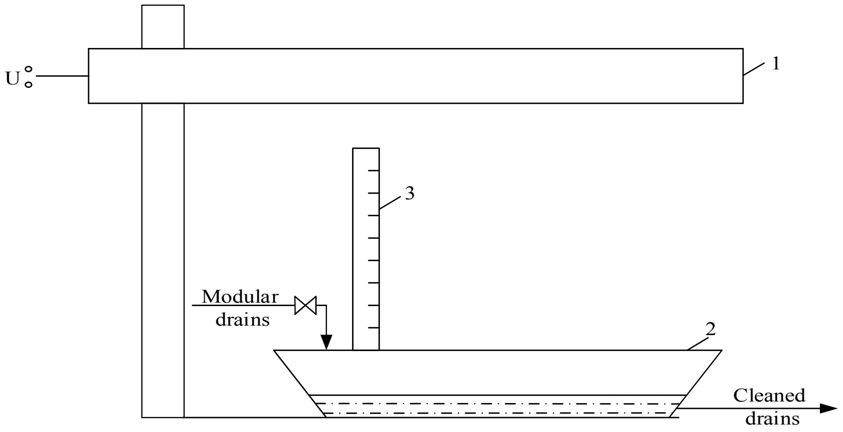

Fig. 1. Scheme of an experimental installation for the process of water disinfection: - ultraviolet lamp, 2 - liquid tray, 3 - way rack

The research results are presented in Fig. 2

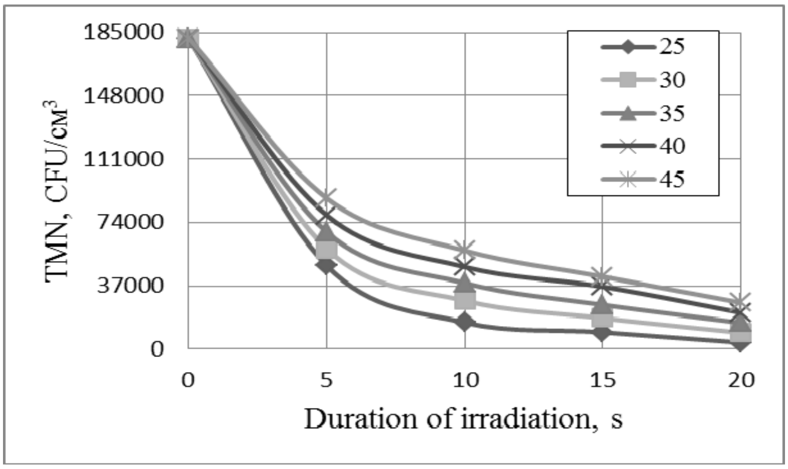

Fig. 2. Dependence of TMN on the duration of irradiation UV-radiation and different thickness of the drainage layer (mm)

Studies have shown that with irradiation of 20 s and a thickness of 25 mm water, TMN is 3757 CFU / cm^3, and the duration of irradiation of 20 seconds and the thickness of the water layer of 45 mm was 27097 CFU / cm^3.

The degree of efficiency of the process of disinfection of wastewater is the degree of purification, which is determined by the formula:

$$N_m = \frac{NM_0 - NM_1}{NM_0} = 1 - \frac{NM_1}{NM_0} \qquad (1)$$

where NM$_1$ - number of microorganisms remaining in water after the action of UV, CFU / cm^3; NM$_0$ - number of microorganisms that were in water before the start of its radiation, CFU / cm^3.

Data shown in Fig. 2, were processed according to the dependence (1). The obtained results are presented in Fig. 3

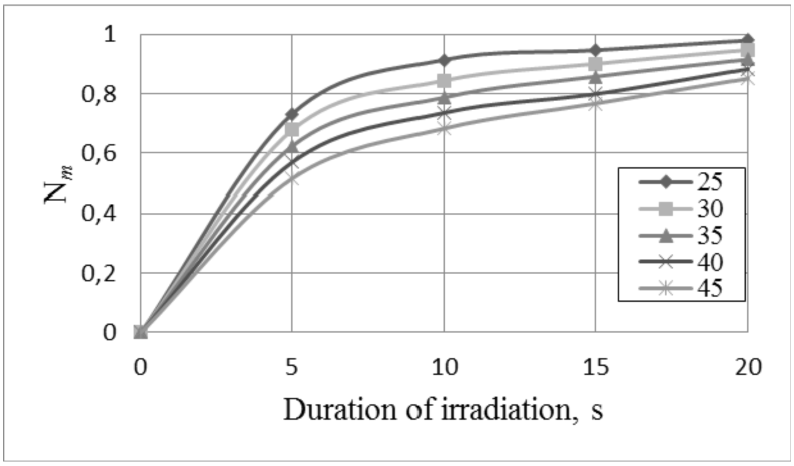

Fig. 3. Dependence of the degree of purification on the duration of irradiation for sewage in municipal sewage treatment plant №2 for different thickness of the liquid layer (mm)

The above data indicate that the degree of purification for municipal sewage treatment plant №2 sewage in the limits of a layer of liquid from 25 mm to 45 mm at 20 s with radiation decreased from 0.9793 to 0.8508.

Conclusion

Investigation process disinfection of water using UV-radiation from municipal water treatment plant №2 of Lviv showed that under the condition of 20 c irradiation and thickness of the water layer 25 mm, the TMN is 3757 CFU / cm^3, while the duration of radiation is 20 seconds and the thickness of the water layer 45 mm, this value amounted to 27097 CFU / cm^3. Under the condition of 20 s with irradiation and thickness of the water layer of 25 mm, UV treatment allowed to reduce the level of the MI by 48 times, while the irradiation time was 20 s and the thickness of the water layer was 45 mm – 7 times. The application of this method is effective and allows the implementation of this process to disinfection wastewater at the sewage treatment facilities of the city of Lviv.

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Influence of Nitrogen Oxides on the Process of Absorption of Greenhouse Gases by Chlorophyll-Synthesizing Microalgae

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Abstract – The influence of nitrogen oxides on the CO_2 uptake rate by chlorophyll-producing microalgae of Chlorella type was investigated. Experimental dependences of microalgae concentration growth over time under certain values of nitrogen oxides concentration in the culture medium were obtained. The mathematical model of microalgae biomass growth depending on nitrogen oxides concentration was developed. Based on the solution of the mathematical model and the obtained experimental data, the concentration of nitrogen oxides for the maximal microalgae growth was determined.

Keywords – nitrogen oxides (N_xO_y), chlorophyll-synthesizing microalgae, biomass growth, mathematical model, optimum concentration.

Introduction

Nowadays, climate change on the Earth makes the world scientific community and world leaders of the states worry. One of the ways to solve this problem is to reduce the concentration of CO_2 in the atmosphere by incorporating the photosynthetic properties of plant organisms in industrial environments. This is one of the methods of biological purification, which is based on the ability of chlorophyll-synthesizing microalgae to involve to the metabolism schemes the substances that cause environmental pollution, using them for nutrition in the process of their life [1].

In the case of fuel combustion, in addition to carbon dioxide (CO_2) and sulfur (SO_2), a large amount of nitrogen oxides (N_xO_y) is formed, which is subsequently oxidized to NO_2 by the air. When it comes to the purification of industrial gas emissions with chlorophyll-synthesizing microalgae, it is important to determine the effect of nitrogen oxides on the processes of carbon dioxide absorption by microalgae.

From literary sources it is known that the concentration of nitrogen oxides that adversely affects the flora is within the range of 0.17 - 0.35 mg/m^3 [2]. Therefore, it was important to investigate the concentration of harmful effects on microalgae of the Chlorella type and, therefore, research within these concentrations was the impetus for our work.

Description of the problem

The object of the laboratory research was Chlorella - the culture of green microalgae. Since nitrogen dioxide is absorbed by micro-algae in the form of anion NO_3^-, for the study of the effect of nitrogen oxides on the growth of chlorophyll-synthesizing microalgae, an anion with the concentration of 1,7 mg / m^3 was added to the first volume, 3,4 mg / m^{3} - to the second, 8,5 mg / m^3 - to the third , 15,6 mg / m^{3} – to the fourth, 34 mg / m^3 to the fifth, and 68 mg / m^3 to the sixth one.

The growth of biomass chlorophyll-synthesizing microalgae under these conditions was determined by a photo-colorimetric method using a blue light filter according to Bouguer-Lambert-Ber.

Since the optical density is proportional to the concentration of algae, which is confirmed by the calibration graph, therefore the experimental data on the accumulation of algae biomass depending on the time within the studied nitrogen oxide concentration (N_xO_y) correspond to the value of optical densities [3].

Based on the results of experimental data and calculation values, graphically dependent changes in the concentration of algae cells in time at the appropriate concentrations of nitrogen oxides (NxOy) in a solution under the conditions of their single injection were obtained (Fig.1, Fig.2).

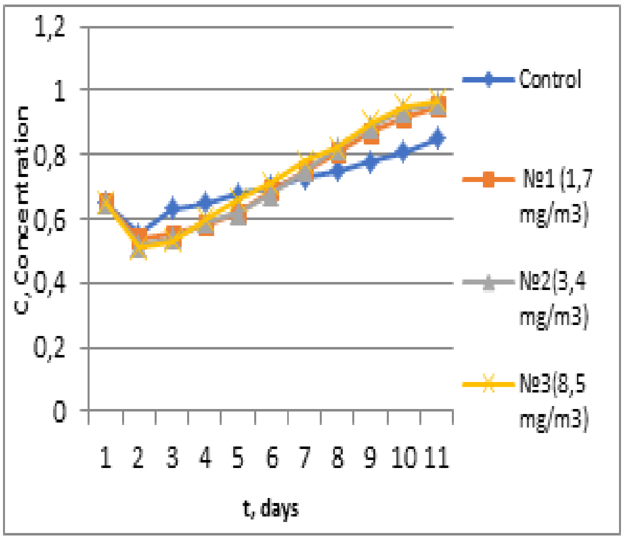

Fig. 1. Dependence of the change in the concentration of cells of algae in time at appropriate concentrations NO_3^-

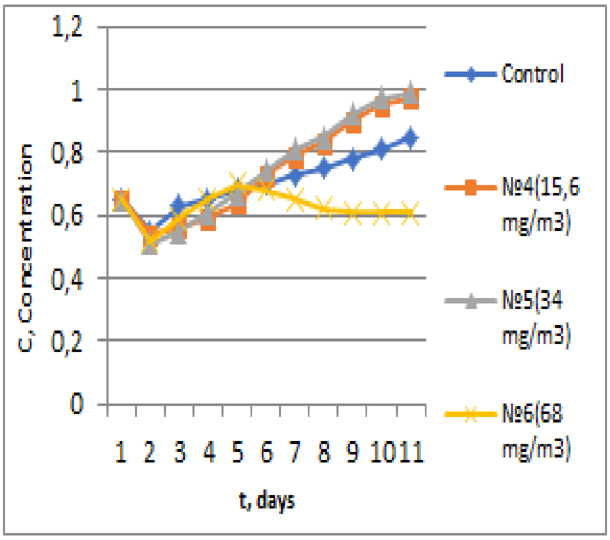

Fig. 2. Dependence of the change in the concentration of cells of algae in time at appropriate concentrations NO_3^-

The main goal of the work should be to find the critical concentration of NO_3^- at which a harmful effect on microalgae will come.

The mathematical formulation of the model for the growth of microalgal biomass under the condition of the presence of nitrogen oxides is to achieve a maximum of their growth, with a further reduction is the system of equations (Eq.1):

$$\begin{cases} \frac{dC}{dx} = k_1 C - k_2 C \\ \frac{dC}{dx} = k_1 C; \qquad ;(1) \\ x = 0, C = C_o; \end{cases}$$

where, x – concentration of nitrogen oxides; C- concentration of algae in a suspension; κ_1, κ_2 - coefficient of growth of biomass of algae.

The decision of the mathematical model has the form (Eq.2):

$$x_{\max} = \frac{\ln k_2 - \ln k_1}{(k_1 + k_2)}; \ (2)$$

Under these circumstances, calculating the growth factors for algae - k, according to experimental data of studies, it is always possible to calculate and predict the values of nitrogen oxide concentrations, which maximize the growth of microalgae in the absorption of carbon dioxide and to forecast equipment for the implementation of the technological process in practice.

Conclusion

A mathematical model of the growth of microalgae colonies in the absorption of carbon dioxide has been constructed under the presence of nitrogen oxides. Based on the decision of the mathematical model and the experimental results obtained, the calculated value of the optimum concentration of N_xO_y for the growth of microalgae of the Chlorella type is established. In addition, the solutions made will allow in the future to predict equipment for the implementation of the technology of absorption of greenhouse gases, provided N_xO_y is present.

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Recycled Sewage Sludge as Part of Organic-Mineral Fertilisers – a Comprehensive Solution to the use of Local Raw Materials

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Abstract* – *Combined granular organo-mineral fertilisers with durable action were created. They consist of sewage sludge, ash residues, processing plant waste, humic substances. Obtained granular organo-mineral fertiliser enabled to enhance mineral nutrition, especially phosphoric, the main grain culture – winter wheat and corn.

Keywords – organo-mineral fertiliser, aeration station, wastewater sludge, sewage sludge, phosphoric nutrition, plant waste, corn.

Introduction

Nowadays, the problem of municipal wastewater sludge treatment and disposal has high ecological and economic significance [1]. A significant amount (more than 0.5 billion tons) of wastewater sludge have accumulated in the territory of Ukraine. Previously, several directions for their utilisation were proposed [2, 3]. The high content of phosphates in sludge, and especially in redundant sludge, allows us to consider such raw material as a promising component of agrochemically effective fertilisers. Unlike nitrogen and other nutrients, fertilisers are the only source for replenishing phosphorus in the soil. The purpose of our work was to create organo-mineral fertiliser (OMF) from sewage sludge, processing plant waste, humic component and study their influence on the ability of plants to use phosphorus of low solubility phosphates of fertilisers and soil.

Materials and methods

Sewage sludge from Bortnychi wastewater treatment plant, ash residues, processing plant waste, humic substances were used as raw materials for the combined granular organo-mineral fertiliser obtaining. The technological scheme of production of granulated OMF was developed Raw materials and created OMF's were analysed using different physical-chemical methods. Investigation of our OMF's agrochemical efficiency were carried out in vegetation experiment condition on the sandy substrate by routine [4]. The experiment determined the effect of OMF on winter wheat's growth processes, rhizogenic, absorption activity of the root system, in particular, phosphorus compounds from established fertilisers and carry-over of phosphorus plants. Field experiment was putted on dark grey, podzolic soil in Kyiv region according to field research procedure. It was researching the effects of new OMF's preplant on the mineral feeding trends, in particular, phosphorus, corn plant productivity and grain quality ratings (Moscito hybrid).

Results

It was established that new OMF had any toxic elements. Fertilisers have a size that meets the requirements of modern agricultural engineering for their introduction into the soil (granules diameter 2-6 mm). It was established that the carry-over factor of phosphorus by plants in vegetation experiment increased on 51-79% for the use of OMF. High adsorption properties of the new granular OMFs components prevent the chemical binding of phosphorus by soil and promote its mobilisation from hard-to-reach soil phosphates and fertilisers. The loose structure of proposed fertilisers contributes to the adsorption and keeping of soil moisture, which must inhibit the processes of eolation and soils erosion.Data from field studies with corn on dark grey, podzolic soil have confirmed the high agrochemical efficiency of our fertilisers. Corn’s experimental plants for the use of such fertilisers formed a rather powerful root system with increased absorption activity (weight and volume of roots dominated control samples up to 28-41%). Introduction to the fertiliser system of the maize hybrid Mosquito OMF-I and OMF-II had affected the improvement of the structural indices of the crop. The one plant’s grain yield in the experiment increased up to 19-43%, the weight of 1000 grains - 14-37%, the weight of the ear - 60-82% compared to the control. Productivity value in the experiment increased up to 5.1 t/ha and 2.3 t/ha using fertilizers I and II respectively at optimum humidification in the accounting year. The introduction of OMF-I (0.5 t/ha) into the fertiliser system of maize hybrid Mosquito promoted to the formation of grain with an increased content up to 18.6% protein compared to control, which introduced only mineral fertilisers. This can be explained by more efficient re-utilisation of absorbed nutrients by experimental plants and rapid outflow of photoassimilates from leaves to grains.

Conclusion

Thus, due to the efficient utilization of plant wastes and wastewater sludge, granulated OMF have been created. The obtaining granulated OMF’s used on sod-podzol and grey forest soils, which are the most widespread in Ukraine, is ecologically promising and resource-saving, which can solve complex social problems of many regions. The resulting fertiliser technology can be attributed to local fertilisers: they are made from local raw materials, do not require transportation over long distances and can be used in neighbouring farming.

Acknowledgments

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Cleaning of Exhaust Gases with Low Content of Sulfur (IV) Oxide

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Abstract – The influence of Ferrum (II) sulfate ($FeSO_4$) concentration in the absorbent solution and the influence of the process temperature on the efficiency of gas emissions purification in the apparatus with bucket dispersants was investigated.

Keywords – exhaust gases, sulfur (IV) oxide.

Introduction

Gas emissions of sulfur (IV) oxide (SO_2) into the atmosphere occupy the second place (after carbon (IV) oxide) by volume and the first place due to harmful effects on the environment. These emissions can lead to crisis environmental conditions, have unpredictable consequences for the health and life of future generations. Therefore, research aimed at developing technologically efficient and cost-effective technologies for the purification of discharged SO_2-containing gases is relevant and important.

In the balance of industrial emissions of SO_2, the bulk (over 80%) accounts for poor exhaust gases (up to 0.5% SO_2). Utilizing SO_2 from such gases is technologically and technically difficult, economically very costly. Therefore, solving the problem can be achieved by removing SO_2 from cheap reagents and waste from other industries. In previous studies, it has been shown that for the purification of gas emissions with low sulfur (IV) oxide it is expedient to use oxidative methods, but as an oxidizer to use air oxygen [1]. The physical and chemical essence of the process corresponds to the greatest extent to the horizontal absorber with bucket dispersants (HABD), which was developed at the department of CTIS [2].

Theoretical part

The oxidation of SO_2 with oxygen in the gas phase is thermodynamically possible under normal conditions. Despite this, gaseous SO_2 and O_2 do not react directly, since the reaction of $2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$ is characterized by a high activation energy (210 kJ/mol). It can be accelerated by the use of catalysts. Available industrial vanadium catalysts are relatively expensive, with an optimal temperature of at least 410 °C. Therefore, the neutralization of SO_2 by its catalytic oxidation in the gas phase is economically inappropriate. Therefore, practical interest is the oxidation of SO_2 by oxygen in aqueous, catalytically active solutions. In this aspect, the Ferrum ions are of considerable interest, the source of which may be iron sulfate ($FeSO_4 \times 7H_2O$), which is the withdrawal of many industries.

The reactions that take place can be expressed by the following stoichiometric equations:

$$2FeSO_4 + O_2 + SO_2 \Leftrightarrow Fe_2(SO_4)_3. \quad (1)$$

$$Fe_2(SO_4)_3 + SO_2 + H_2O \Leftrightarrow 2FeSO_4 + 2H_2SO_4. \quad (2)$$

In total, this process can be expressed by the following reaction

$$2SO_2 + O_2 + 2H_2O \Leftrightarrow 2H_2SO_4. \quad (3)$$

These processes are equilibrium, so, changing the conditions, you can direct the process to the desired side. The standard electrode potential of the $Fe^{3+} \rightarrow Fe^{2+}$ system is equal to 0.77 V, while the system $O_2+4H^++2e \rightarrow 2H_2O$ equals 1.23V. Since the electrode potential of the oxidizer is greater than that of the reducing agent, the reaction will take place, and the driving force of the process will be 0.46 V (1.23-0.77). Consequently, the liquid-phase oxidation of SO_2 by oxygen in the presence of Fe^{2+} i Fe^{3+} ions is theoretically possible, characterized by a rather significant driving force.

Experimental part

Experimental studies were carried out on a laboratory installation of an enlarged type. The installation consisted of three main units: the preparation of a gas mixture for the preparation of the absorbent solution and absorption. As an absorber, HABD was used. Laboratory HABD - is a horizontal cylindrical apparatus (internal diameter 500, length 300 mm), made of organic glass. A bucket dispersant was placed on the bottom of the apparatus on a horizontal shaft.

The influence of temperature on the course of the process was studied in the range 35-50 °C. The concentration of $FeSO_4$ was changed within the range of 0 ... 0.2 mol/l, and the SO_2 content in the gas mixture - within the limits of 3.5 ... 19.5 g/m^3.

It was established that the dependences of the absorption and oxidation steps of the absorbed SO_2 in the liquid phase on the concentration of Ferrum (II) sulfate have an extreme character with a maximum equal to the concentration of $FeSO_4$ 0.025 mol/l. The presence of a maximum can be explained by the fact that the process occurs statically: at first, Fe^{2+} ions are oxidized to Fe^{3+}, which, in turn, oxidizes chemosorbed SO_2 to sulfate ions. Consequently, an increase in the concentration of Fe^{2+} ions will have a positive effect on the oxidation processes. However, the increase in the concentration of $FeSO_4$ leads to an increase in the acidity of the solution (decrease in pH), and this will negatively affect the absorption of O_2 and SO_2 by the absorbent solution.

An increase in the oxidation rate of sorbed SO_2 can be achieved by an increase in temperature, which for this process, obviously, will have some optimal value. This is explained by the fact that, on the one hand, with increasing temperature the solubility of gases decreases, which leads to a decrease in the concentration of their hydrated forms, and, on the other hand, the increase in temperature leads to an increase in the reaction rate (1, 2). It is established that the optimum temperature of the process of purifying gases from SO_2 by solutions of Ferrum (II) sulfate is in the region of 313 K. In addition, the region of extremum on these dependencies is more pronounced in the case when the contact time in the apparatus is lower. Thus, up to 313 K, the increase in the oxidation rate of sorbed SO_2 is greater than the relative reduction in the solubility of gases.

Conclusions

Studies have helped to identify regularities of SO_2 oxidation with oxygen in aqueous solutions of iron sulfates and determine optimal spacing $FeSO_4$ concentration and temperature are respectively equal to 0.015 ... 0.03 mol/l and 312 ... 318 K.

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Wet Integrated Flue Gas Cleaning

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Abstract – A wet method for flue gas cleaning from ash and sulfur dioxide based on a wet venturi scrubber has been proposed An increase in the specific consumption of irrigation water in the Venturi tube of 0.7 kg/m3 and higher will allow reaching an output dust concentration below 20 mg/m^3, while reducing the energy consumption of flue gas for droplet evaporation and fresh water consumption. The use of ammonia in wet desulfurization technology will allow the use of an existing wet scrubber while observing the SO_2 limit concentration of 200 mg/m^3.

Keywords – wet scrubber Venturi, flue gas, dust removal, wet ammonium desulfurization, ammonia sulfate.

Introduction

The Association Agreement between Ukraine and the European Union in 2014 includes an obligation for our country to comply with the requirements of the Directive 2010/75/EU on industrial emissions [1]. This is especially true of thermal power plants, which are among the main sources of pollutants of the environment. The actual level of dust concentrations in the flue gases of TPPs of Ukraine is in the range of 400–1500 mg/m^3, depending on the type of ash collector used. The concentration of sulfur dioxide is determined by the sulfur content in the fuel and is in the range of 2500–6500 mg/m^3. In November 2017, the Order of the Cabinet of Ministers of Ukraine approved the National Plan of Emission Reduction from large combustion plants [2], which provides for the stading implementation of the requirements of Directive 2010/75/EU. After December 31, 2018, on existing combustion plants, the final concentration of dust should be no higher than 20 mg/m^3, and the emission limit value of sulfur dioxide in dry flue gases will be 200 mg/m^3. To ensure such high requirements, the efficiency of the dust cleaning system should be at least 99.85% with the initial dust content of the flue gas (DG) stream 30 g/m^3, and to reduce the SO_2 emission, it is necessary to ensure the binding of sulfur dioxide with an efficiency higher than 96%.

In Ukraine, a significant part of coal-fired boilers (up to 30% by thermal capacity) of thermal power plants and combined heat and power plants are equipped with wet scrubbers with Venturi tubes for flue gas cleaning. In Fig. 1 is a schematic of a wet Venturi scrubber. The flue gas after the boiler air preheater passes through the Venturi tube. In the Venturi nozzle, water drops form, which are the coagulation centers of dust particles. After the Venturi tube, the flue gas flow and droplets of water and dust slurry tangentially enter the bottom of the wet scrubber. Due to the centrifugal force of the suspension drops will be deposited on the wall of the scrubber, on which to prevent drip entrainment with a water supply, a stable water film is provided. The ash pulp is discharged from the low part of the scrubber.

The technology of particulate matter removal in wet scrubbing is included in the European list of the Best Available Techniques [3]. These ash collectors also partially reduce sulfur dioxide emissions (up to 10%) due to the solubility of SO_2 in water and the presence of alkaline earth components in the ash.

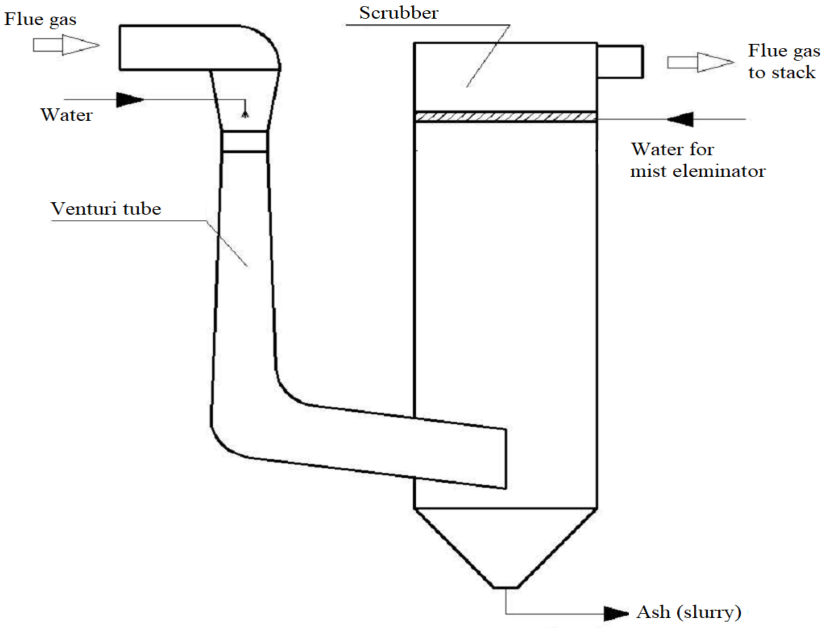

Fig. 1 – Wet scrubber with Venturi tube

Under the conditions of the dense layout of equipment of existing TPPs and CHPs of Ukraine, there is often no room for placing new ash collectors and desulfurization systems. One of the solutions to this problem may be the modernization of existing wet Venturi scrubbers to the apparatus for complexly cleaning of flue gas from dust and sulfur dioxide, according to the requirements of Directive 2010/75/EU.

Material and Methods

Optimization of the structural parameters of wet scrubbers has limited possibilities for a significant increase in dust collection efficiency. A significant improvement in dust collection in wet scrubbers can be achieved mainly only by increasing the water consumption for irrigation of the Venturi pipes.

Traditionally, the specific consumption of irrigating water in the Venturi pipe was limited to 200 g/m^3 by the condition that the flue gas reaches a dew point and the danger of corrosion of equipment located downstream. In addition to dust cleaning, the modernization of wet Venturi scrubber involves the introduction of desulfurization systems, the most effective of which are wet-type plants [3,4].

There is a practical experience of using intensive irrigation regimes of scrubbers with Venturi pipes [5]: at boiler No. 12 of the Togliatti CHP in 2007, modernization was carried out to transfer wet ash collectors to intensive irrigation, which increased the efficiency of ash collection to 99.5 % due to an increase in the irrigation density of the Venturi coagulators by 3.5 times. However, it also required heating of the purified flue gases by no less than 10 °C.

An increase in the flow rate of the irrigating water will influence the working efficiency and the selection of the operating parameters of the wet ash collector. An increase in the flow rate of irrigating fluid will affect the dynamics of evaporation of droplets in an environment with varying moisture content. From the diameter of the droplets depends on the efficiency of the capture of particles of fly ash droplets in the Venturi tube. An increase in the irrigation consumption will lead to an increase in the hydrodynamic resistance of the wet ash collector, which entails the need to increase the performance of ID fan.

Estimation of the efficiency of trapping solid particles in a wet Venturi scrubber can be performed on the basis of a mathematical model of particle deposition on water droplets in a Venturi tube [6,7], the adequacy of which is confirmed by experimental data [5,8,9], using the formula^

$$\eta = 1 - \exp\left(-\frac{3}{2}\frac{q_w}{D_d \cdot \rho_l} \cdot \int_0^L \eta_\Sigma(x) \cdot \left|\frac{v_p(x) - v_d(x)}{v_d(x)}\right| dx\right), \qquad (1)$$

where q_w – irrigation density of gas-dust flow, kg/m^3; η_Σ – precipitation coefficient of solid particles with a diameter d_p on spherical droplets with a diameter D_d; ρ_l – water density, kg/m^3; v_p – velocity of ash particle with diameter d_p, m/s; v_d – velocity of drop with diameter D_d, m/s; L – Venturi tube length, m; x – coordinate along the Venturi tube axis, m.

To remove sulfur dioxide, it is proposed to apply, on the basis of the existing wet scrubber, a wet ammonium sulfate technology [3, 10], which has a high desulfurization efficiency, obtained as a by-product of ammonium sulfate (mineral fertilizer).

Results and discussion

The results of the calculation of the efficiency of cleaning flue gases from fly ash for different sizes of dust particles and different consumption of irrigating water in the Venturi tube are presented in Figure 2.

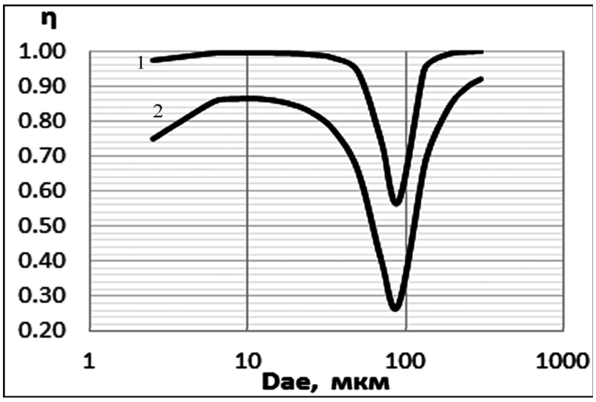

Fig. 2 – Fractional efficiency η of flue gas cleaning in the Venturi with q_w = 0.42 kg/m^3 (curve 1) and q_w = 0.16 kg/m^3 (curve 2).

Curve (2) shows the efficiency of dust collection by droplets of 150 µm in diameter in the Venturi tube at an irrigation density of q_w = 160 g/m^3. Curve (1) corresponds to dust collection efficiency with the same drops at q_w = 420 g/m^3. With an increase in irrigation consumption, the efficiency of trapping dust ranging in size from units to tens of microns is high and approaching unity (100%). The dips in curves (1) and (2) are explained by the convergence of the values of the aerodynamic diameters of dust particles and droplets; here, $|(v_p - v_d)/v_d| \to 0$, and particles with droplets move in the gas stream without colliding. However, drops and particles of this size (more than 40 µm) are effectively captured further downstream in the scrubber droplet separator [6]. The main task is to trap small particles in the Venturi tube; these are mainly PM10 and PM2.5 particles, which are poorly captured by most ash collectors, with the exception of fabric filters. As follows from Fig. 2, the most effective particles of fly ash of this class can be captured in the Venturi tube with drops at an irrigation density of more than 400 g/m^3.

The dynamics of the main thermophysical parameters of a heterogeneous flow in an environment with varying moisture content was studied. In this case, the effect of droplet size on efficiency was considered. Calculations showed that droplet sizes in Venturi scrubbers to achieve an acceptable degree of dust cleaning should fall in the range of diameters: 70 µm < D_d <300 µm [11]. However, even in this range, the characteristic droplet size should be distinguished, according to which, according to the data of mathematical and engineering calculations, when designing wet Venturi scrubbers, which is also confirmed by the test results of industrial ash collecting plants with Venturi pipes at a number of TPPs, the highest ash particles are observed. These are drops with a diameter of about 150 μm. Therefore, it is preferable that the maximum distribution of droplets in size, formed by the nozzles that irrigate the scrubber, falls on drops of such diameter. Drops of this size under the same conditions evaporate less than, for example, droplets with a diameter of less than 50–70 μm, which does not require corrections to the equations of their motion in gas as a result of changes in the size of droplets during their evaporation. An important conclusion from the comparison of the calculation results for cases of moderate and increased irrigation water flow is that the evaporation of droplets suppressed at high irrigation levels leads to a lower resulting moisture content of flue gas (Fig. 3)

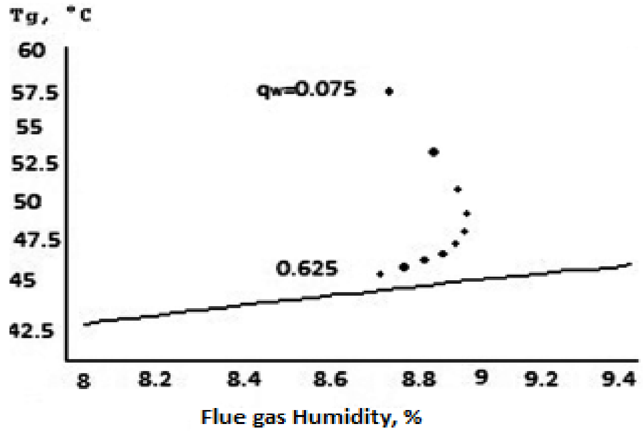

Fig. 3 – Saturation curve (solid) and points showing temperature and vapor content in flue gas at the Venturi scrubber outlet with irrigation densities $q_w = 0.075$; 0.185; 0.24; 0.295; 0.35; 0.405; 0.405; 0.46; 0.515; 0.625; kg/m^3.

This is not an obvious conclusion at first glance, but with an increase in the amount of water injected into the Venturi tube, the humidity of the flue gases at the scrubber outlet actually decreases. This is due to the increased energy consumption by flue gases to heat the flow of droplets in the Venturi tube to the dew point with a higher irrigation density, therefore less energy will be used to evaporate the droplets [11]. Therefore, at the exit from the venturi tube, the flue gas temperature will be higher than the water temperature.

In the existing scheme of a wet venturi scrubber, pulp consisting of water (90%) and captured ash (10%) is transported by a pump through pipes to the ash dump. It is proposed to change the scheme for obtaining on the territory of TPPs the ownership of ash to 15% as a by-product with its subsequent sale to consumers (Fig. 4). In the existing scheme of a wet Venturi scrubber, the pulp consisting of water (90%) and captured ash (10%) is transported by pumping through pipes to the ash dump. It is proposed to change the scheme for obtaining in the territory of TPPs ash ownership by up to 15% as a by-product with its further sale to consumers (Fig. 4). For this purpose, it is planned to use a hydrocyclone and a vacuum filter in order to separate the solid phase from the liquid and obtain ash as a product at the outlet. In this case, there is no need to transport the ash suspension to the ash landfill.

To remove sulfur dioxide, it is proposed to place in the wet scrubber a system of volumetric spraying of droplets of an aqueous solution of ammonia and ammonium sulfate against the flow of flue gas. The regulating grid must equalize the velocity fields after the venturi. In solution makers, ammonia forms an acid salt with sulfur dioxide by the reaction:

$$NH_3 + H_2O + SO_2 = NH_4HSO_3 \qquad (2)$$

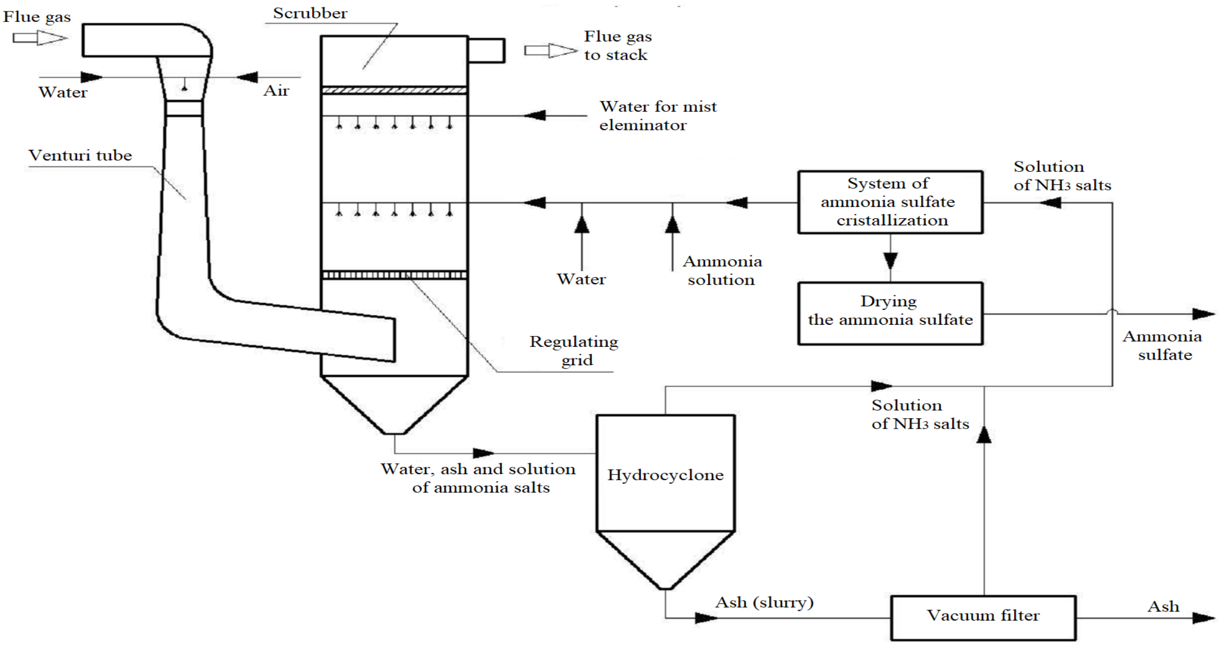

Fig. 4 – Scheme of the upgraded wet Venturi scrubber

When the droplets move to the lower part of the scrubber, the acid salt in the acidic medium will be oxidized with oxygen from the air supplied additionally with water to the Venturi nozzle to form ammonium sulfate by the reaction:

$$2\ NH_4HSO_3 + O_2 = (NH_4)_2SO_4 + SO_2 + H_2O \qquad (3)$$

The reactions (2) and (3) are protolytic and flow almost instantly.

Since all ammonia salts are water-soluble, after the hydrocyclone and the vacuum filter, ammonium sulfate solution will be in the liquid phase. In the system of ammonium sulfate crystallization of there will be an accumulation of its concentration in the solution until precipitation of $(NH_4)_2SO_4$ crystals. After drying, the white powder of ammonium sulfate (mineral fertilizer) will be supplied to the consumer.

The unsaturated ammonium sulfate solution together with fresh water and ammonia water is returned to the wet scrubber. The specific consumption of an aqueous solution of ammonia and ammonium sulfate in a wet scrubber is determined by the solubility of sulfur dioxide and is about 3 kg/m3 of flue gas.

Conclusions

1. Wet Venturi scrubber can be the basis for the installation of complex cleaning of flue gases from ash and sulfur dioxide. To achieve a dust concentration below 20 mg/m3, it is proposed to increase the specific water consumption in the Venturi tube to 0.7 kg/m3. This reduces the energy costs of evaporation of the droplets and the consumption of fresh water. The optimal drop size is 150 µm.
2. To reduce SO_2 emissions subject to the limit value of 200 mg/m^3 of sulfur dioxide concentration, it is proposed to use ammonium sulfate technology by spraying an ammonia solution with a flow rate of up to 3 kg/m^3 in a wet scrubber and obtaining an ammonium sulfate solution.
3. A scheme has been proposed for an updated wet Venturi scrubber with a system for obtaining ash with a humidity of up to 15% and a system of obtaining the ammonium sulfate as a by-product, allowing to abandon the hydraulic ash disposal system.

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Features of Semi-Dry Ammonium Desulfurization

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Abstract – Semi-dry ammonium desulfurization technology is proposed to meet the requirements of Directive 2010/75/EU on reducing sulfur dioxide emissions and obtaining dry product - ammonium sulfate. The peculiarity of this technology is the presence of a gas-phase reaction of sulfur dioxide with ammonia along with the absorption of SO_2 in drops of ammonia water. The efficiency of the absorption of sulfur dioxide by gaseous ammonia (up to 90%) has been experimentally proved, subject to the presence of water vapor in the gas, the volume concentration of which should exceed the volume concentration of ammonia.

Keywords – flue gas, semi-dry desulfurization, sulfur dioxide, ammonia, ammonium sulfate.

Introduction

The issue of environmental protection in the combustion of fuel is becoming increasingly urgent and priority. One of the main pollutants of atmospheric air is sulfur dioxide SO_2, which is the product of oxidation of sulfur as a fuel component. The absence of flue gas cleaning from sulfur dioxide at the Ukrainian TPP leads to significant emissions of it to the atmosphere - more than 1 million tons per year. The direction of European integration of Ukraine's development is set the task of compliance with the requirements of the European Directive 2010/75/EU on industrial emissions [1], which defines emission limit values of sulfur dioxide from large combustion plants (200 mg/m^3 – for existing plants and 150 mg/m^3 – for new ones). Therefore, the task of reducing sulfur dioxide emissions by developing efficient, low-cost and compact desulfurization technologies and in which will be formed a useful product, is urgent.

In the world in branch power industry become the most widespread the wet limestone desulfurization with forced oxidation, which is able to meet the requirements of Directive 2010/75/EU, has high capital and operational costs, uses natural mineral as a sorbent and forms as byproduct gypsum (building material) [2]. Semi-dry lime technology is characterized by lower capital costs. They use as a sorbent a more expensive lime and the byproduct is a dry mixture of calcium sulfite, calcium sulfate and unused lime, which has very limited application.

An alternative to calcium desulfurization techniques can be ammoniacal technologies with the use of ammonia as a sorbent and the production of ammonium sulfate, which is a mineral fertilizer [2]. Wet ammonium sulfate technologies have high efficiency of binding of sulfur dioxide (+ 98%), lower operating costs, but the process of obtaining ammonium sulfate from solution is technologically difficult [3].

The proposed semi-dry ammonium desulfurization method has low capital costs (as semi-dry technology), low operating costs, and high efficiency of SO_2 removal (as ammonia technology), and will be formed the dry sulfate of ammonium. In fig. 1 shows a scheme of semi-dry desulfurization using ammonia water as a sorbent [4].

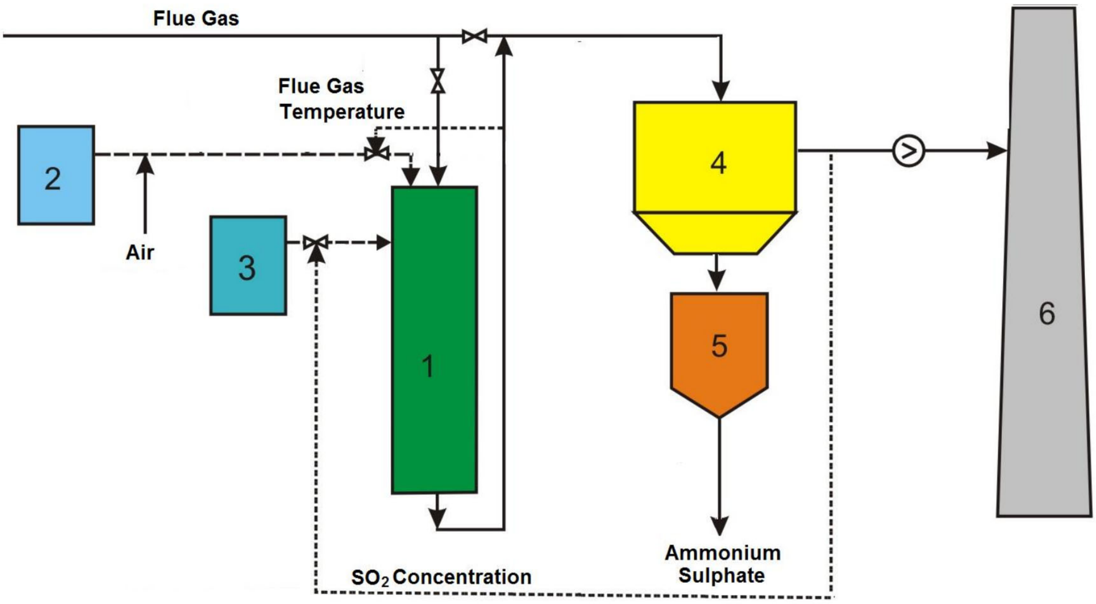

Fig. 1 – Schematic diagram of the semidry ammonium desulfurization
1 – reactor; 2 – technical water tank; 3 – ammonia water tank; 4 – fabric filter;
5 – ammonium sulfate silo; 6 – chimney

Flue gas after dust precipitation is introduced into the reactor, which is usually supplied with drops of ammonia and technical water. In drops of ammonia solution NH3, dissociation occurs with the formation of ammonium cation [5]:

$$NH_3 \times H_2O \leftrightarrow NH_4OH^+ + OH^- \quad (1)$$

Sulfur dioxide as a component of flue gas is dissolved in water, with the formation of mainly anion of hydrosulfite [5,6]:

$$SO_2 + H_2O \leftrightarrow HSO_3^- + H^+ \quad (2)$$

$$HSO_3^- \leftrightarrow SO_3^{-2} + H^+ \quad (3)$$

In the presence of oxygen in flue gas, the reaction of conversion of the anion of hydrosulfite into anion sulfate with the release of sulfur dioxide occurs [6]:

$$2\ HSO_3^- + O_2 \leftrightarrow SO_4^{-2} + SO_2 + H_2O \quad (4)$$

Ammonium cation will react with anions of hydrosulfite and sulfate by reactions:

$$NH_4OH^+ + HSO_3^- \leftrightarrow NH_4HSO_3 + H_2O \quad (5)$$

$$2\ NH_4OH^+ + SO_4^{-2} \leftrightarrow (NH_4)_2SO_4 + H_2O \quad (6)$$

Simultaneously with the chemical reactions in the reactor, there are processes of heat and mass transfer between hot flue gas and cold droplets - heating and evaporation of moisture due to the heat of flue gas. By the definition of semi-dry technology in the reactor there should be complete evaporation of the introduced moisture, and the temperature of the treated flue gases should be at least 10 °C above the water dew point [2, 4, 6]. After evaporation of the moisture, NH_4HSO_3 and ammonium sulfate molecules $(NH_4)_2SO_4$ will form aerosols which will precipitate on the surface of bags of fabric filter in the form of particles of up to 5 microns in size, with the reaction of conversion of ammonium hydrosulfite to ammonium sulfate

$$2\ NH_4HSO_3 + O_2 \leftrightarrow (NH_4)_2SO_4 + H_2O \quad (8)$$

The part of the ammonia enters the flue gas from drops of ammonia water in the molecular form. The ammonia concentration in the gas phase depends on the content of ammonia NH_3 in the drops of ammonia water and their temperature [7]. The formation of aerosols of ammonia and sulfur dioxide of submicron size occurs in flue gas containing sulfur dioxide. The main component of such aerosols is amido-ammonium sulfite $(NH_3)_2 \times SO_2$ [8] which in the presence of water vapor and oxygen in the flue gas on the surface of the bags of fabric filter is converted to ammonium sulfate:

$$(NH_3)_2 \times SO_2 + H_2O + ½\, O_2 = (NH_4)_2SO_4. \qquad (9)$$

A certain part of the gaseous ammonia is absorbed by the drops of technical water due to a high absorbing property of NH_3 [7]. The end-product of the absorption of sulfur dioxide and ammonia in the drops of technical water is ammonium sulfate.

Material and Methods

The peculiarity of ammonium semi-dry desulfurization is the presence of a gas-phase reaction between ammonia and sulfur dioxide. To test this hypothesis, a series of experimental studies was conducted.

In fig. 2. the scheme of experimental laboratory installation for the study of gas-phase reactions is presented. Model gases $N_2 + SO_2$ and $N_2 + NH_3$, as well as pure N_2, are fed to a gas heater in which the separated gases are heated. Next, the model gases $N_2 + SO_2$ and $N_2 + NH_3$ are directed to the gas-phase reactor. Nitrogen passes through a humidifying chamber, where it adds a water vapor.

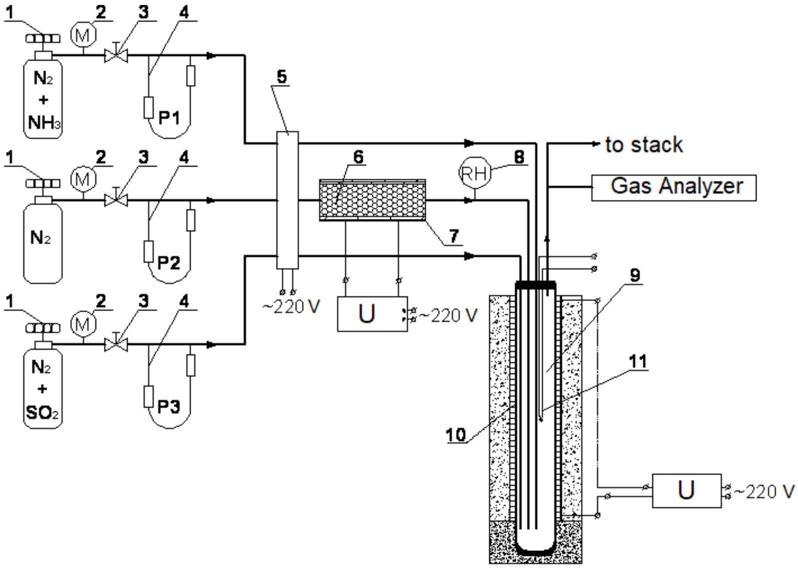

Fig. 2 – Scheme of installation of gas-phase reaction of ammonia and sulfur dioxide in humid conditions.
1 – balloons with nitrogen and mixtures; 2 – gearboxes; 3 – fine control valves; 4 – rheometers; 5 – gas heater; 6 – evaporator; 7 – heater; 8 – a moisture meter; 9 – reactor; 10 – reactor heater; 11 – thermocouple.

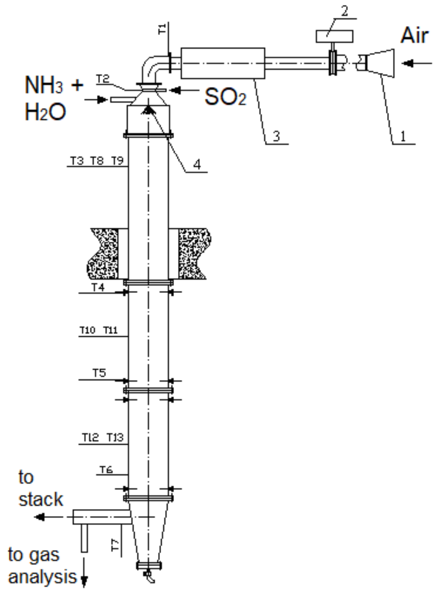

Fig. 3 – Scheme of installation of semi-dry cleaning
1 – air flow regulator,
2 – micromanometer, 3 – electric furnace for air preheating,
4 – ammonia solution atomizer,
T1-T13 – thermocouple.

Experiments were conducted in two modes: mode 1 (the water vapor content in the gas mixture is determined by the final moisture contained in the technical nitrogen balloon) and mode 2 (the water vapor content in the gas mixture is determined by the flow of water supplied to the humidifying chamber). The temperature of the gas mixture in the reactor was higher than 100 °C, which eliminates the absorption of sulfur dioxide in droplets.

A series of experiments were carried out to obtain a complex result of absorption of ammonia sulfur dioxide, in which a solution of ammonia was introduced into the hot gas stream containing sulfur dioxide using a pneumatic nozzle. That is, in the absorption of sulfur dioxide ammonia, dissolved in water droplets, and ammonia, which passed through the desorption from the solution into the gas phase, was involved.

Experimental pilot installation for the study of the process of semi-dry cleaning of flue gases from sulfur dioxide (Fig. 3) is a vertically placed cylindrical reactor with a height of 2600 mm and an internal diameter of 320 mm. To the outlet pipe of the reactor is connected a ID fan, which creates the movement of air through the reactor in the chimney. The air velocity in the reactor is regulated by the change in the passage through the channel. The heating of the air is made using an electric furnace, which is a ceramic tube in which the heating elements are located. The reactor and the supply path of hot air outside have thermal insulation.

Results and discussion

As a result of experiments of the gas-phase reaction of ammonia and sulfur dioxide, the average values of SO_2 concentration after the reactor were obtained and the removal efficiency of sulfur dioxide in mode 1 (with the content of water vapor in the gas mixture determined by moisture contained in the technical nitrogen cylinder) and mode 2 (with the content of water vapor in the gas mixture is determined by the flow of water vapor formed in the chamber of moisture) [9]. In each of the modes, three experiments were performed with a mole ratio of NH_3/SO_2 = 0.89; 1.5; 2.23. According to the results of the research, the dependence of the efficiency of the sulfur dioxide removal on the ratio NH_3/SO_2 was obtained (Fig. 4).

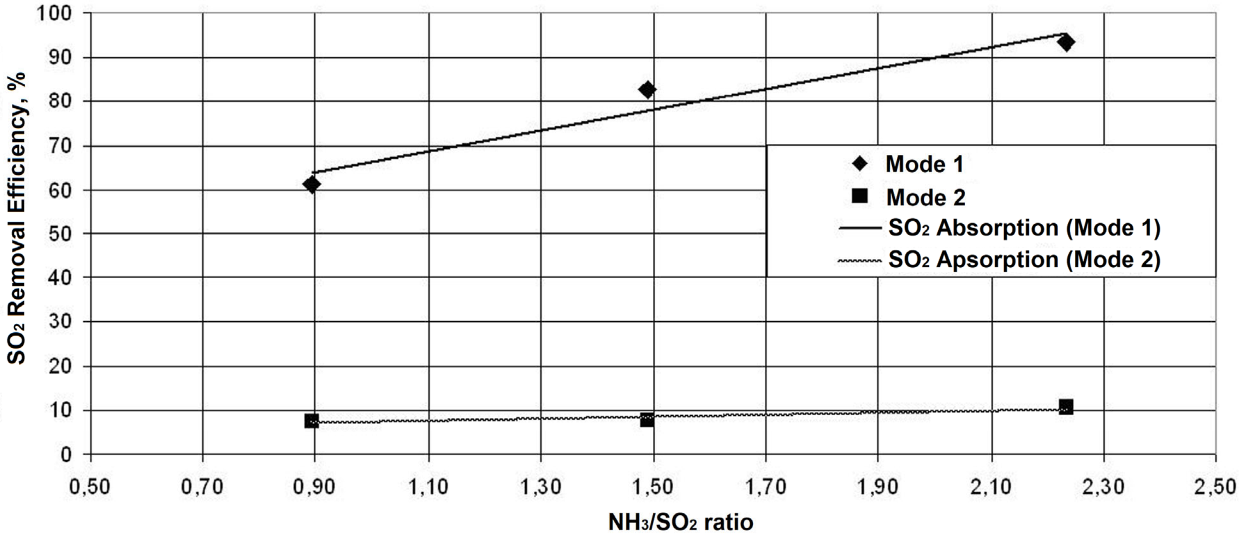

Fig. 4 – Dependence of the efficiency of sulfur dioxide reduction from the molar ratio NH_3/SO_2

These experiments showed that the increase in the water vapor content (change in the molar ratio of H2O / NH3 from 0.21 to 1.08) significantly improves the efficiency of binding of sulfur dioxide to gaseous ammonia (change from 7.9% to 82.8% at the initial molar ratio NH_3/SO_2 = 1.5). This is due to the catalytic effect of water vapor on the reaction of coupling sulfur dioxide with ammonia in the gas phase.

Thus, it has been experimentally proved, that for the gas-phase absorption of sulfur dioxide ammonia, the volumetric concentration of water vapor should exceed the volume concentration of ammonia.

The results of tests of the complex absorption made it possible to experimentally confirm the presence of gas-phase absorption by ammonia and determine the total efficiency of absorption of sulfur dioxide by a solution of ammonia. In all experiments, when the ammonia solution is fed to the reaction zone, the absorption of sulfur dioxide is observed. Input and output parameters of experiments are shown in Table 1.

Table 1

Parameters of experiments on the installation of semi-dry cleaning

Parameter	A	B	C
The gas temperature at the inlet to the reactor, °C	95.4	95.4	88.7
Concentration of SO_2 at the reactor inlet, ppm	600	850	1000
Model gas consumption, l/min	2526	1656	1284
Mass consumption of ammonia solution, g/s	1.72	1.72	1.72
NH_3 mass concentration in solution, %	1.24	1.24	1.24
Initial molar ratio NH_3/SO_2	1.5	1.6	1,7
Concentration of SO_2 at the reactor outlet, ppm	179	215	239
Desulfurization efficiency, %	70.2	74.7	76.1

The obtained data showed that the total efficiency of sulfur dioxide reduction is at the level of 70-76% with a molar ratio of NH_3/SO_2 = 1.5-1.7, which excludes the release of ammonia in ambient air.

The efficiency of removing SO_2 can be greatly increased by increasing the inlet temperature of the gas phases. This will increase the amount of ammonia solution introduced into the reactor and dissolved sulfur dioxide in the liquid. Another leverage for increasing efficiency (by 20%) is an increase in the molar ratio of NH_3/SO_2 to stoichiometric (up to 2).

Conclusions

1. In order to comply with the requirements of Directive 2010/75/EU, it is necessary to promptly implement desulfurization technologies that ensure high efficiency of removal of sulfur dioxide (97% +), are economical and form a useful by-product. Such technology is semi-dry ammonium desulfurization to yield dry ammonium sulfate.
2. The peculiarity of semi-dry ammonium desulfurization is the presence of sulfur dioxide in drops of ammonia solution and the gas-phase reaction between ammonia and sulfur dioxide. Experimentally, the degree of removal of sulfur dioxide (up to 90%) was obtained by reacting SO_2 with ammonia in the gas phase. The determining condition for this effect is the presence in the gas medium of water vapor, the volume concentration of which must exceed the volume concentration of ammonia.
3. Experimental studies of complexly semi-dry ammonium desulfurization confirmed the high efficiency of this technology, even in conditions of low input temperature of gas and molar ratio NH_3/SO_2 less than 2.

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Estimation Method of Greenhouse Gases Emissions at Thermal Power Plants

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Abstract* – *A method for calculating CO_2 emissions from coal combustion at the TPP is developed on the basis of carbon emission factors, taking into account the heat value of coal and heat losses due to the presence of unburnt carbon in ash. The values of CO_2 emissions at Ukrainian TPPs are obtained. Specific emissions of carbon dioxide are closely 1100 g CO_2/kWh, which correlates with high specific consumption of fuel for electricity production at the TPP.

Keywords – environment, thermal power plant, flue gases, carbon dioxide, emission factor, calorific value.

Introduction

On October 31, 2018 the Cabinet of Ministers of Ukraine approved the draft Law of Ukraine "On the Basics of Monitoring, Reporting and Verification of Greenhouse Gas Emissions", aimed at fulfilling the obligations assumed by Ukraine under the Association Agreement between Ukraine and the EU. This Law is a framework, it defines the legal and organizational frameworks for the functioning of the monitoring, reporting and verification of greenhouse gas emissions (MRV). It is ready Draft Resolution of the Cabinet of Ministers of Ukraine "On Approval of the Procedure for the Monitoring and Reporting of Greenhouse Gas Emissions". The basis of the MRV system is a set of methods for calculating GHG emissions, but in Ukraine does not have a single appropriate methodology that would be based on the use of the emission factor that takes into account the heat value of fuels, as required by Directive 2003/87/EC

One of the largest sources of greenhouse gas emissions is thermal power plants (TPPs). At the Ukrainian TPPs in recent years 13–19% of the total volume of anthropogenic emissions of greenhouse gases is thrown out. In 1990, they emitted 50 million tons of carbon dioxide, in recent years – about 60 million tons per year. Mainly, it is carbon dioxide that is the main greenhouse gas that is produced by combustion of organic fuels. The main factors that determine the large emissions of carbon dioxide at the TPP are the volume of coal consumption and high specific fuel consumption for electricity production (see Table 1).

Table 1

Volume of coal consumption and specific fuel consumption for electricity prodaction at Ukrainian thermal power plants in 2013–2017

Показник	Years				
	2013	2014	2015	2016	2017
Coal consumption, mln. t	36.8	32.5	26.7	29.2	22.4
by A and P coals	17.8	14.5	8.4	12.1	4.4
by G and DG coals	19.0	18.0	18.3	17.1	18.0
% in fuel balance	98.0	98.3	98.0	98.3	98.7
Specific consumption, g CE/kWh	394.8	397.7	400.8	403.7	402.6

A – anthracite, P – semiathracite, G – bituminous coal, DG – subbituminous coal.

Coal consumption at the TPP has been decreasing in recent years, mainly due to a reduction in the use of anthracite and semianthracite, but its volume remains high – tens of millions of tons. In the fuel balance of Ukraine's TPPs, the share of coal is very high – more than 98 % [1]

In addition, all Ukrainian TPPs, in accordance with the Monitoring and Reporting Procedure for greenhouse gas emissions, belong to Category B plants, in which the average annual emission of greenhouse gases exceeds 500 kt of CO_2. Coal at these thermal power plants refers to a "substantial material flow". When applying the calculation methods for estimating CO_2 emissions from burning "significant material flows" for Category B plants, the following techniques should be used which allow obtaining accuracy levels of at least 2.5%. Fuel oil and natural gas at Ukrainian coal-fired thermal power plants are "minor" and "minimal material flows", the amount of CO_2 emissions generated during their combustion is less than 5 kt and 1 kt of CO_2 per year, respectively. For their calculations, the accuracy levels are allowed to be less than 5.0 % and 7.5 %, respectively, which are achieved with the application of standard techniques. Therefore, the issue of creating a methodology for calculating CO_2 emissions from coal combustion, which takes into account the heat value of fuel and allows to obtain levels of accuracy less than 2.5%, is of interest.

Material and Methods

With a known the elemental composition of coal, according to the standard method, it is possible to determine the gross emission of carbon dioxide in dry flue gas generated by coal combustion. Information on carbon dioxide emissions from combustion of fossil fuels is obtained either by continuous measurements of CO_2 concentrations and flow rates of flue gas or calculated methods based on data of fluels consumption, composition of used fuel and characteristics of power boilers. For the organization of continuous continuous measurements of concentrations of pollutants and volumetric flow rates of flue gas, it is necessary to use measuring equipment, which today is not available at most of Ukrainian thermal power plants

Calculated methods for determining CO_2 emissions from fuel combustion are based on the use of the emission factor and the degree of oxidation of carbon in a fuel in a boiler [2]:

$$E_{CO_2} = 10^{-6} k_{CO_2} \cdot B \cdot LHV \text{, (1)}$$

where E_{CO_2} – CO_2 gross emissions, kt; k_{CO_2} – emission factor of CO_2, g/GJ; *LHV* – low hear value of fuel, MJ/kg; *B* – fuel consumption during the time (year), kt.

The emission factor characterizes the ratio of mass of the emitted substance at the power plant into the atmosphere to the unit of energy emitted during combustion of the fuel. It depends on many factors. There are two emission factors - generalized and specific. In the presence of both coefficients, it is necessary to use a specific one.

The generalized CO_2 emission factor is the average specific emission value for a specific type of fuel. It does not take into account the features of the chemical composition of fuel. The CO_2 specific emission factor is the specific emission value, which is determined for a power plant, taking into account the individual characteristics of the fuel and the specific characteristics of the combustion process. The CO_2 specific emission factor for coal can be written as [2]:

$$k_{CO_2} = \frac{44}{12} \cdot \frac{C^r}{100} \cdot \frac{10^6}{LHV} \varepsilon_C = 3{,}67 k_C \varepsilon_C \text{, (2)}$$

where C^r – carbon content in coal as row, %; *LHV* – low heat value of coal, MJ/kg; ε_C – oxidation degree of fuel carbon; k_C – emission factor carbon, g/GJ.

Oxidation degree of fuel carbon ε_C is defined according [3]:

$$\varepsilon_C = 1 - \frac{q_4}{C^r} \cdot \frac{LHV}{Q_C}, \quad (3)$$

where q_4 – heat losses due to present of unburnt carbon in ash, %; Q_C – heat value of coal equivavent (CE), 32,68 MJ/kg.

According to our calculations, the oxidation degree of fuel carbon ε_C with an accuracy of 0.6% can be determined by the formula [3]:

$$\varepsilon_C = 1/(1 - q_4/100). \quad (4)$$

The specific carbon emission factor k_C is the ratio of the carbon content of the coal to coal heat value:

$$k_C = \frac{C^r}{100} \cdot \frac{10^6}{LHV}. \quad (5)$$

In the absence of data on the carbon content of coal and its combustion heat, for estimation calculations, generalized emission factors of carbon k_C, g/GJ, may be used, or in the Ukrainian national document GKD 34.02.305-2002 (hereinafter – GKD) or in the report of the Intergovernmental Panel on Change Climate (IPCC). It should be noted that European guidelines and methodological documents on the definition of greenhouse gases have determined that the values of carbon dioxide specific emission factors depend on the country of coal production, and it is recommended to use the national values of these factors.

Consequently, the calculation of the specific carbon emission factor is based on the use of carbon content in coal C^r, the values of lower heat values LHV and heat losses due to present of unburnt carbon in ash at the power plant q_4. But in real terms, the coal batches supplied to the TPPs are accompanied only by a technical analysis in which only such fuel characteristics are provided, which do not allow to calculate a specific carbon emission (directly by standard method). Therefore, the purpose of the work was to developing the engineering method for calculating the CO_2 emissions generated by combustion of coal at the TPP, according to the technical analysis, taking into lower heat value *LHV*.

The engineering method of calculation was developed on the basis of 140 certificates for coal and coal products from mines and cleaning factories of Donetsk coal basin, for samples of coal of the anthracite (A), semi-anthracite (P), gas (G) and gas flame (DG) types, with a *LHV* range from 16.1 to 31.3 MJ/kg [4]. The certificates were drafted and approved by the state enterprise "UkrNDIvuhlezbahacennia". According to the certificates, the elemental composition for each fuel sample was determined and the carbon specific emission factors k_C were calculated.It is established that for coal of the A, P, G and DG types the dependence of specific coal emission factors k_C, g/GJ on the heat value of coal *LHV*, MJ/kg, has a linear character: $k_C = a - b \cdot LHV$, where *a* and *b* are coefficients, depending on the of coal type. For coal of the P type, the dependence of specific carbon emission factors on the heat of combustion of coal was not detected.

Table 2 summarizes the results of calculations, namely the dependence of the values of carbon specific emission factors k_C on the lower heat value of coal, MJ/kg, relative errors, δ, %, the range of the obtained values of carbon specific emission factors and the values of the generalized carbon emission factors for charcoal of grades A, P, G and DG. In addition, for comparison in Table 2 shows the values of the generalized carbon emission factors k_C from the national control document GKD 34.02.305-2002 and the IPCC report. It is evident that the values of fuel-aggregate carbon emission factors differ significantly from national and European carbon emission factors.

The analysis of the results shows that for coal of the P, G and DG types the values of generalized carbon emission factors from different sources are in the range of values obtained from calculations of specific carbon emission factors (see Table 2, the maximum and minimum values are given). For coal of the A type, the values of the carbon emission factors are much higher. The error of calculating the specific emission factor of carbon for the dependencies given in Table 2 is less than 2.5%, which meets the requirements for monitoring, reporting and verification of greenhouse gas emissions from power industrial installations. It should be noted that fuel combinations of coal of the A and P types are burned at the Ukrainian TPPs. The use of the values of the generalized carbon emission factors from Table 2 is associated with some errors, because in the official report TPP is not provided with information on mass part of coal of this or that type. Therefore, for the estimated calculations of carbonspecific emission factors for the combustion of coal mixtures of A and P types, it is proposed to use the dependence $k_C = 28900 - 50\times LHV$ [4].

Table 2

Specific and generalized carbon emission factors for Ukrainian coal of different types

Carbon emission factors k_C, g/GJ	Coal types		
	A	P	G and DG
Specific carbon emission factor:			
got dependence	$k_C = 29900 - 40\times LHV$	26450	$k_C = 26800 - 55\times LHV$
δ, %	0.97	0.90	2.39
maximum value	29735	26805	27292
minimum value	28200	25934	24116
Generalized emission carbon factors:			
our calculations	28760	26450	25630
are given in the	28160	26050	25180
shown in the IPCC report	26810	no data	25800

Results and discussion

According to Table 2 data and formula (4), the values of specific carbon emission factors and gross carbon dioxide emissions, kt, were calculated from the combustion of coal at the Ukrainian TPPs. The calculations used information on the quality, the cost of coal supplied to the TPPs, and the values of q_4 from the official TPP statistics - 3Tech.

Table 3 shows the results of these calculations for coal-fired power plants and 5 power generating companies of Ukraine for 2017. Table 3 also shows the fuel types burned at the TPP and the percentage of coal in the fuel balance of the TPP. For comparison, in Table 3 also results of the corresponding calculations according to the method of GKD 34.02.305-2002 on the carbon generalized emission factors without considering the information on the heat value of coal.

GHG gross emissions from coal combustion at Ukraine's TPPs in 2017 amounted to 44.4 million tons. The use of carbon emission factor calculations taking into account the lower calorific value of coal has given the value of gross CO_2 emissions at Ukraine's TPPs in 2017 by 800 kt more than by using generalized emission factors from GKD 34.02.305-2002.

In order to determine the exact values of specific and gross emissions of carbon dioxide at the TPP, the calculations should take into account the emissions generated by the combustion of coal, natural gas and fuel oil:

$$E_{CO_2}^{\text{fuel}} = E_{CO_2}^{coal} + E_{CO_2}^{\text{fuel oil}} + E_{CO_2}^{\text{gas}}, \quad (6)$$

where $E_{CO_2}^{\text{fuel}}$ – gross emissions of CO_2 formed during combustion of fuel at the TPP in a year, kt; $E_{CO_2}^{coal}$ – gross emissions of CO_2 formed during combustion of coal at the TPP in a year, kt; $E_{CO_2}^{\text{fuel oil}}$ – gross emissions of CO_2 formed during combustion of fuel oil at the TPP in a year, kt; $E_{CO_2}^{\text{gas}}$ – gross emissions of CO_2 formed during the combustion of gas at the TPP in a year, kt.

Table 3

Specific carbon emission factors and gross CO_2 emissions from coal combustion at Ukraine's TPPs in 2017

Power generating companies of Ukraine / TPPs	Types of coal	Coal		q_4, %	Results of calculation			
		LHV, MJ/kg	*B*, kt		considering LHV and q_4		according GKD considering q_4	
					k_C, g/GJ	$E_{CO_2}^{coal}$, kt	k_C, g/GJ	$E_{CO_2}^{coal}$, kt
PJSC Donbasenergo			1048.4			2510.4		2457.9
Slov'yanska	A	24.32	1048.4	2.88	27684	2510.4	27105	2457.9
PJSC Centerenergo			3047.7			6313.6		6196.6
Vuhlegirska	G, DG	21.86	1935.6	0.22	25598	3963.1	25180	3898.5
Trypilska	A, P	21.73	464.1	6.36	27814	963.2	27105	938.6
Zmiyivska, в т.ч.		22.48	648.0					
No. 1–4	A, P, G	22.42	259.4	1.53	27779	556.3	27105	545.6
No. 5–6	A, P, G	22.42	315.6	2.66	27779	674.0	27105	660.5
No.7–10	A, P	22.95	73.0	7.89	27982	157.0	27105	153.3
PJSC DTEK Dniproenergo			4756.3			9676.5		9502.8
Kryvorizka	P	23,42	1220.8	6.14	26450	2602.7	26050	2563.4
Prydniprovska, в т.ч.		23.29	689.4			1498.2		1466.1
No. 7–10	A, P, G	23.29	572.9	6.17	27736	1248.3	27105	1221.9
No. 11–14	A, P	23.28	116.5	9.42	27736	249.9	27105	244.2
Zaporizka	G, DG	20.90	2846.1	0.34	25650	5575.6	25180	5473.3
PJSC DTEK Zakhidenergo			8391. 0			16423.6		16125,8
Burshtynska	G, DG	21.06	4441.0	0.97	25642	8708.0	25180	8551.2
Dobrotvirska, в т.ч.		21.15	1348. 8		25642	2641.3	2641,3	2594.2
No.7–8	G, DG	21.12	790.4	1.58	1544,3	1544.3	25180	1516.7
4×50 MW		21.21	558.4	1.44	1097,0	1097.0	25180	1077.5
Ladyzhinska	G, DG	20.83	2601.2	0.42	25655	5074.3	25180	4980.4
DTEK Skhidenergo Ltd.			5182.0			9461.0		9301,4
Kurakhivska	G, DG	18.07	3922.7	1.9	25806	6577.3	25180	6417.7
Luhanska	A, P	23.84	1259.3	5.45	27708	2883.7	27708	2883.7
Total, of them			22425.4			44385.1		43584.5
for grades of A, P		23.54	4874.9			11845.5		11669.1
G, DG		20.45	17550.5			32539.6		31915.4

Calculations of $E^{\text{fuel oil}}_{CO_2}$ and $E^{\text{gas}}_{CO_2}$ were performed using formulas (1) and (2) using the values of carbon generalized emission factors k_C, g/GJ, from GKD 34.02.305-2002: for fuel oil $k_C = 21100$ g/GJ, for gas $k_C = 15300$ g/GJ. The calculations also used information on the quality, consumption of fuel oil and gas supplied to the TPP, and the value of q_4 from the official statistics of TPP – 3Tech.

Table 4 presents the results of calculations of CO_2 gross emissions from fuel combustion at coal-fired power plants of Ukraine and separately for coal, natural gas and fuel oil. Data are provided for power generating companies of Ukraine. The obtained values coincide with operational data of Ukrainian TPPs. The calculation error for CO_2 gross emissions at the TPP was 1.3%.

Table 4

Estimated and available values of gross CO_2 emissions from fuel combustion at Ukraine's TPPs in 2017

Power generating companies of Ukraine	Results of calculation, kt				TPP data $E^{\text{fuel}}_{CO_2}$, kt	δ, %
	$E^{coal}_{CO_2}$	$E^{\text{fuel oil}}_{CO_2}$	$E^{\text{gas}}_{CO_2}$	$E^{\text{fuel}}_{CO_2}$		
PJSC Donbasenergo	2510.4	0.05	21.2	2531.6	2576.0	1.7
PJSC Centerenergo	6313.6	23.4	40.2	6377.2	6130.5	4.0
PJSC DTEK Dniproenergo	9676.5	45.4	92.3	9814.3	9692.1	1.3
PJSC DTEK Zakhidenergo	16423.6	29.0	169.9	16622.5	16388.1	1.4
DTEK Skhidenergo Ltd.	9461.0	63.7	26.4	9551.0	9527.5	0.2
Total	44385.1	161.55	350.0	44896.65	44314.2	1.3

According to the developed method, the calculations of gross CO_2 emissions at coal-fired power plants of Ukraine in recent years have been made. Table 5 shows the gross and specific emissions of CO_2 from coal-fired power plants in Ukraine in 2017 and, for comparison, in 2014–2016 [4]. The results are summarized for TPPs, burning coal of the A and P type and coal of G and DG type.

Table 5

Total and specific CO_2 emissions from coal-fired power plants in Ukraine in 2014–2017

TPPs	Supplied electric energy,		Gross CO_2 emissions		Specific CO_2 emissions		Coal *LHV*, MJ/kg	Specific fuel consumption, g/ kWh
	kWh	%	kt	%	g CO_2/ kWh	t CO_2/ t coal		
2014								
Total	62032.7		68114.1		1098.0	2.09	21.9	397.7
TPPs burning A + P	28561.6	46.0	33111.6	48.6	1159.3	2.27	23.4	413.6
TPPs burning G + DG	33471.0	54.0	35002.5	51.4	1045.8	1.94	20.7	387.9
2015								
Total	49397.8		54592.9		1105.2	2.04	21.3	400.8
TPPs burning A + P	15564.5	31.5	19102.4	35.0	1227.3	2.29	23.2	428.5
TPPs burning G + DG	33833.2	68.5	35490.5	65.0	1049.0	1.93	20.4	389.8

2016								
Total	52726.3		60636.2		1150.0	2.07	21.6	403.7
TPPs burning A + P	21454.9	40.7	27534.4	45.4	1283.4	2.28	23.3	423.8
TPPs burning G + DG	31271.4	59.3	33101.8	54.6	1058.5	1.90	20.4	395.6
2017								
Total	40526.1		44896.5		1107.8	2.0	21.1	402.6
TPPs burning A + P	9046.8	22.3	11679.8	26.0	1291.1	2.63	25.9	431.2
TPPs burning G + DG	31479.9	77.7	33216.7	74.0	1055.2	1.85	20.0	391.5

Table 5 shows that the values of CO_2 specific emissions at the TPP are at the level of 1100-1150 g CO_2/kWh. At the TPP burning coal of the A and P type, values of specific CO_2 remissions reach 1200–1300 g CO_2/kWh, that is, by 30 % higher, than at the TPP, burning coal of the G and DG type. This correlates with higher values of the heat value of coal of the A and P type, compared with coal of the G and DG type.

For comparison, this value is 860–940 g CO_2/kWh at the coal-fired power plants of Japan, Europe, and America with the supercritical steam parameters (240–260 bar vapor pressure, such as at coal-fired TPPs in Ukraine) with installed desulfurization and denitrification equipment. At the TPPs with ultra super-critical parameters of steam (pressure more than 280 bar), specific CO_2 emissions are 760–840 g CO_2/kWh [5]. This correlates with high values of specific fuel consumption per 1 kWh of electricity generated at Ukrainian thermal power plants.

Ukraininan TPPs must pay an environmental tax. The environmental tax rate for CO_2 emissions by stationary sources in 2017, according to Article 243 of the Tax Code of Ukraine, was to 0.41 UAH per/t. Estimated total cost of CO_2 emission amounted to UAH 18.55 mln. or EUR 0.62 mln. Since January 1, 2019, the environmental tax rate for CO_2 emissions from stationary sources has been emissions at Ukraine's TPP increased to 10 UAH/t.

Conclusions

Based on the above mentioned the following conclusions can be summarized as follows.

1. The basis of the monitoring, reporting and verification of greenhouse gas emissions is a set of methods for assessing greenhouse gas emissions. Today in the Ukrainian power sector of Ukraine there is no single obligatory methodology for calculating greenhouse gas emissions based on the use of the GHG emission factor and takes into account the heat value of fuels, as required by Directive 2003/87/EC.
2. The method was developed for calculating the CO_2 emissions generated by combustion of coal at the TPP, based on specific carbon emission factors, taking into account the heat value of coal and heat losses due to present of unburnt carbon in ash.
3. The developed method allow to calculate the values of specific carbon emission factors and gross CO_2 emissions at Ukraine's TPPs in 2017. The value of specific CO_2 emissions at the TPP in recent years is 1100 g CO_2/kWh.

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Evaluation of Environmental Risk of Manufacturing Complexes

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***Abstract* – The article presents the implementation of the developed methodology for assessment of environmental safety level and identifying the environmental risk of industrial enterprises at life cycle stages. The proposed approach to environmental safety assessment can be applied not only to existing industrial enterprises but also at the design stage.**

Keywords – assessment, damage, environmental management system, environmental safety, hazard, index, indicator, industrial object, risk.

Introduction

The current trend in the world to assess the impact of environmental factors on human health and environmental impact assessment is the application of risk assessment methodology. This kind of analysis is the most acceptable in managerial decisions, since it allows: to compare the risks of different nature and to identify the most important; to characterize quantitatively the potential and actual damage to human health; determine the priority of existing threats; to formulate an effective strategy and regulation tactics of technological regimes of industrial complexes. It is necessary to recognize that implementation of the risk assessment methodology in the management decision-making practice is constrained, in particular, by the absence of appropriate normative documentation in Ukraine. And there are also rare systematic computer databases that are needed for risk assessment.

Today, the risk is understood as a measure of hazard, but as a hazard distinguish phenomena, processes, actions, or conditions that are characterized by the presence of a potential that can harm human health, lead to death, damage natural environment, lead to loss of anthropogenic material objects. It is necessary to emphasize the probabilistic nature of this concept. There is no single way to measure or quantify risk. Here one should proceed from the available information and resources.

Built on the basis of these requirements, the environmental management system contains all the elements that are essential for a rational attitude to resources in production complexes.

The third edition of the ISO 14001:2015 standard, "Environmental management systems - Requirements with guidance for use" is relevant in world practice in environmental management. The main advantage of the standard is the system approach and the balanced combination of processes that make up the well-known Deming cycle (PDCA, Pan-Do-Check-Act cycle).

Methodology for assessing the environmental safety level of industrial enterprises

When using the risk assessment methodology, it's always important to remember that we are dealing with estimates. In order to properly use these assessments for the development of technical and managerial decisions, for relations with public and administrative bodies, it is very important that the potential degree of uncertainty of these assessments is known. When developing a method for a comprehensive assessment of environmental hazard, it is possible to use different techniques, but one must ascertain whether determined results are unambiguous.

Taking into account the above-mentioned features, it is possible to develop a methodology for assessing the level of environmental safety of industrial enterprises, which can be summarized in the following stages. At the first stage, a system of indices is developed which determines quantitative indicators of industrial ecosystem component's quality or industrial object's state.

Here index is a measure of deviation from baseline (either from a standard, or from a steady state). In this context, the indices that have an absolute value must be given as relative values. In the second stage, the system of indexes is converted to a unified form using the desirability function. In the third stage, an assessment of the environmental (technogenic) risk is determined using dependencies of the "index-risk" method. The number of estimated indices can be very high in the quantitative risk analysis of industrial productions. The presentation of risk reduces this large amount of information, leading it to a managed form. At the fourth stage, the interpretation of the results is carried out [1].

This framework helps implementing the developed methodology for evaluating the level of environmental safety and identifying the environmental risk of industrial enterprises at all stages of life cycle, in particular, in the following techniques and assessment systems:

- methodology for assessment of environmental safety level and impact of industrial objects on the environment at the design stage;
- methodology for assessment of technogenic safety level and the impact of industrial objects on the environment;
- economic, ecological, and social sustainability assessment system of territorial units and industrial objects;
- methodology for assessment of environmental safety level and impact of industrial objects on the environment at the exploitation stage.

Let's consider the basic principles of the mentioned methods. Life cycle stage of production is fundamental in systems of indicators. The conceptual model of the environmental safety of industrial objects in designing is presented in Fig. 1 [2].

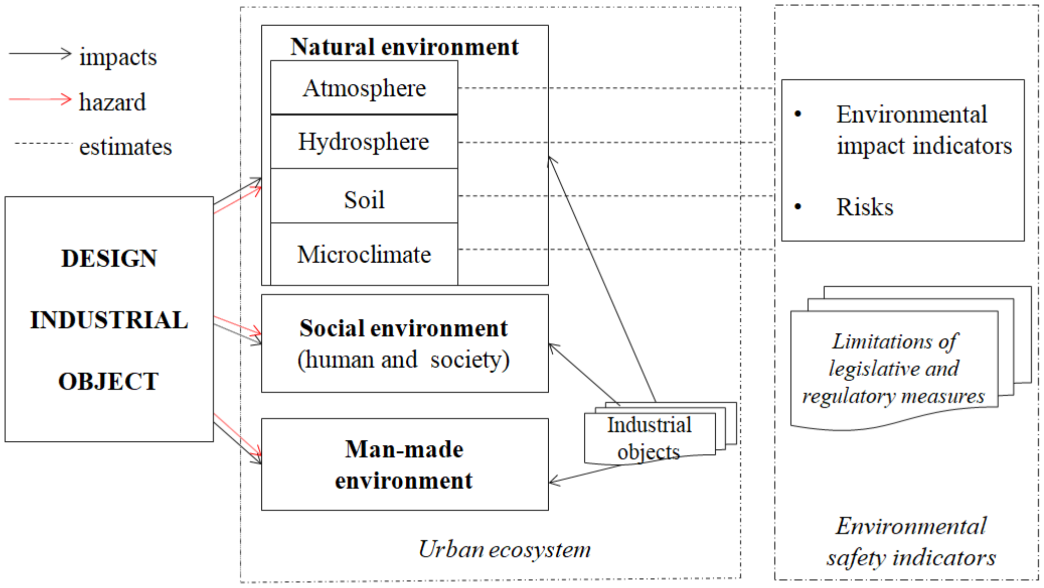

Fig.1. A conceptual model of the environmental safety assessment of a design industrial object.

Considering ecological safety as a complex system it is possible to propose as ecological safety indicators of designed industrial object - risk indicator and environmental impact indicators of an industrial object which is implemented as a model of risk assessment using the indicators unification method:

$$R_E = \sum_{i=1}^{m} r_i, \quad r_i = a_i \cdot e^{b_i \cdot I_i}, \quad r_{i,k} = c_i \cdot e^{d_i \cdot I_{i,k}} \quad (1)$$

where R_E is an integrated environmental risk; r_i is the risk of changes in the state of the *i* environmental medium (atmosphere, surface waters, soils); *a*, *b* are estimated coefficients related to environmental medium specifics; *e* is exponential function; I_i is index of estimation of ecological hazard level of an impact on the *i* environmental medium; $r_{i,k}$ is risk of changes in the state of the *i* environmental medium by *k* substance (individual effects assessment for each substance); *c*, *d* are estimated constants, which are related to the specifics of a substance of environmental medium; $I_{i,k}$ is an index of estimation of the level of environmental hazard of *k* substance impact on the *i* environmental medium [3].

The coefficients associated with environmental medium specifics are obtained using the nonlinear regression method for the following environment pollutions: chemical (atmosphere, surface waters, soils); noise, infrasonic; ultrasound electromagnetic; vibration; radioactive. Levels of assessment scale for environmental hazard impact on environmental medium (*I*) and levels of the scale of classification of the risk environmental changes (*r*) are adopted. Assessment of the level of environmental changes risk for *i* environmental medium is carried out in accordance with the proposed scale (Table 1) [4].

Table 1

Classification of levels of environmental changes risk

Risk Level	Risk Value R_E ,r_i
unacceptable	$>10^{-6}$
conditionally acceptable	$10^{-6} – 10^{-7}$
acceptable	$10^{-7} – 10^{-8}$
absolutely acceptable	$< 10^{-8}$

On the basis of the obtained value, a decision is made on the acceptability of production complex project for each specific pollutant of the relevant environmental medium and in general [5].

The assessment methodology for technogenic safety level and industrial objects environmental impact is summarized by the principal scheme of index assessment of the hazard of potentially environmentally and technologically hazardous objects (Fig. 2). This methodology is based on the calculation of two interrelated safety indicators: the relative hazard index and the regional hazard index, which are determined on the basis of estimated aggregative indicators. Aggregative indicators characterize various aspects of enterprise safety.

The index of relative hazard of industrial enterprises is a complex indicator that takes into account:

- risk of technological operations execution (including storage and warehousing);
- possible damage from the occurrence of unplanned incidents (accidents), caused both internal and external factors;
- relative hazard of enterprise location at a certain industrial site, taking into account the social and geographical features of enterprise location, which affect the possible damage as a result of emergency situations or accidents.

For a compactly located enterprise (within a single enclosed territory, regardless of its size), the resulting index of hazard is the maximum index of a number of indices that are estimated for certain types of hazards. For territorially distributed enterprises, hazard indices of their individual parts (sources of hazard) are estimated as for individual enterprises.

The risk index of hazard source functioning at an industrial plant is a combined indicator that takes into account the guaranteed lifetime of equipment operating in hazardous operations, as well as endogenous and exogenous factors that significantly affect its safety. The exogenous factor is the factor (state parameter) capable of, under the influence of natural or man-made processes, not related to the activity of the given enterprise (production cycle of this source of hazard), obtainment a value that significantly affects enterprise safety. Endogenous factors include factors (state parameters) that characterize the technological process, its equipment, and quality of service, the change of which can significantly affect industrial enterprise safety. Endogenous factors are, first of all, technological parameters of production processes, which significantly differ from the environmental parameters. Exogenous factors can be of an anthropogenic nature (transport accidents that can lead to dangerous disturbances of the normal technological process), and of spontaneous nature (earthquakes, landslides, hurricanes, and so on) [3].

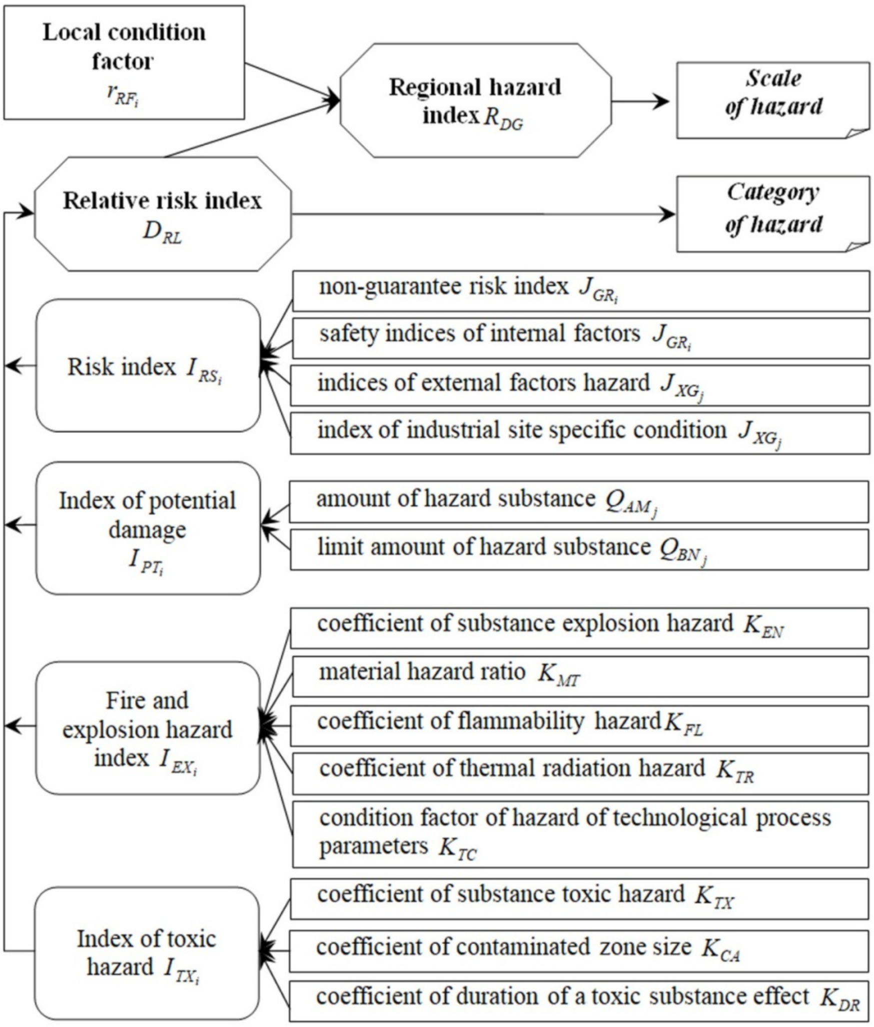

Fig. 2. Principal scheme of index estimation of the hazard of industrial enterprises.

During the development of methodology, normative and legal documents on natural environmental protection, human health, environmental safety in Ukraine, other countries and internationally were taken into account.

It should be noted that the basis of assessment of potential damage is the limits of storage of hazardous substances (compounds) and the maximum amount of hazardous substances that may be present in the enterprise in fact. Indices of potential damage are estimated for individual sources of hazard, taking into account their possible interference.

In order to take into account the hazard of the presence of fire and explosive substances on the investigated facility, an index of fire and explosion hazard is assigned.

The presence of chemicals on an industrial site involves the obligatory account of the toxic hazard associated with the impact of chemical pollution on the environment.

The assignment of a potentially hazardous object to a certain category of hazard is carried out in accordance with the obtained values of unitary fire and explosion indices I_{EX_i}, toxic hazard I_{TX_i}, as well as risk indices I_{RS_i} and index of potential damage I_{PT_i}, using which the unitary index of relative hazard D_{RL_i} is estimated. Ranking of objects according to the degree of hazard is carried out on a five-level scale: up to 0.20 - safe; from 0,20 to 0,37 - low hazardous; from 0.37 to 0.63 - moderate hazard; from 0.63 to 0.80 is hazardous.

When calculating the index of relative hazard, the features of its location are not taken into account. The location of a potentially hazardous facility was considered only from the point of view of the negative impact of the environment on the safety of industrial enterprise operation. But this did not take into account the possible negative impact on the environment in the event of an accident, depending on a specific location of the object.The threat from a potentially hazardous object located in a densely populated region will be much greater than that of a similar facility located in a less populated area. The possibility of spreading harmful substances when they enter the reservoirs and rivers may also be a hazard.Dependence for the calculation of the index of relative hazard can be supplemented by new indices that are used in other methods, which provides the opportunity to comprehensively assess the level of hazard of an industrial object according to different criteria and taking into account its specificity.

The methodology for assessing the level of technogenic safety and the impact of industrial objects on the environment practically implements the system of sustainability indices under the regimen mode, or a set of indicators of the technogenic safety assessment of the enterprise and represents as Eq.2.

$$\begin{cases} D_{RL} = \max\limits_{i=1,n}(D_{RL_i}) \\ D_{RL_i} = \exp\left\{-\dfrac{1}{4}\left[\begin{gathered}\exp\left(-1,9+2,4\cdot I'_{PTi}\right)+\exp\left(-1,7+0,01\cdot I'_{RSi}\right)+ \\ +\exp\left(-2,1+0,01\cdot I'_{EXi}\right)+\exp\left(-1,9+0,01\cdot I'_{TXi}\right)\end{gathered}\right]\right\} \\ I'_{RS_i} = \dfrac{J_{GR_i}/\left(1-J_{SP_i}\right)}{\prod\limits_{k=1}^{m_{EN}} J_{EN_k}\cdot\left[\sum\limits_{j=1}^{m_{XG}}\left(1-J_{XG_j}\right)\right]/m_{XG}^2}, I'_{PT_i} = \dfrac{\sum\limits_{j=1}^{n} Q_{AM_j}/Q_{BN_j}}{n} \\ I'_{EX_i} = K_{EN}\cdot K_{MT}\cdot K_{FL}\cdot K_{TR}\cdot K_{TC}, I'_{TX_i} = K_{TX}\cdot K_{CA}\cdot K_{DR}\cdot K_{TC} \end{cases} \quad (2)$$

where D_{RL} is index of relative hazard of compactly located industrial enterprise; D_{RL_i} is index of relative hazard of a separate source; n is number of sources of hazard of an industrial enterprise; I'_{RS_i} is index of risk of the *i* source of hazard, taking into account the guaranteed lifetime of the equipment, endogenous and exogenous factors; I'_{PT_i} is index of potential damage of *i* source of hazard and is determined by the limits of standard and maximum quantities of hazardous substances (compounds); I'_{EX} is the fire and explosion hazard index of the *i* source of hazard takes into account the hazard from the presence of fire and explosive substances; I'_{TX_i} is the toxic hazard index of the *i* source of hazard takes into account the toxic hazard of the substance under the influence of technological parameters of the process, the duration of its impressive action and the size of the possible zone of contamination [6].

Index of regional hazard is calculated by the expression:

$$R_{DG} = D_{RL} \cdot \sum_{i=1}^{l} r_{RF_i} \quad (3)$$

where r_{RF_i} is the coefficient of taking into account local characteristics; *l* is the number of regional factors taken into account.

The coefficients of taking into account local features include:

- the condition factor of the population exposed to the risk of a hazardous object;
- the condition factor of the value of the environment (protected or resort area);
- the condition factor of the possibility of the transboundary impact of a hazardous enterprise (taking into account the distance to the border with other states);
- the condition factor of the possibility of distributing accidental discharges of hazardous substances in the aquatic environment; it is determined by the affiliation of the industrial site sources of hazard to one or another water basin (regardless of the proximity of the coastline and mandatory for all industrial enterprises).

Results of hazard and risk assessment

The regional hazard index is a comprehensive estimate and determines the expediency of placing a potentially hazardous object on the selected industrial site in connection with the possible consequences (economic, environmental, social, etc.) of accidents at industrial enterprises. The classification of industrial enterprises according to this indicator takes place in accordance with the nature of the enterprise's hazard: less 1 - local; from 1 to 10 - regional; more than 10 - state.

Thus, the use of indices enables assessing the hazard of industrial production without the development of emergency scenarios and monitoring the work conditions and equipment failures, as well as the search for analogs.

To obtain values in probabilistic estimates (technogenic risk) it is enough to use their connection with the function of desirability by the expression:

$$risk = a \cdot e^{b \cdot d} \quad (4)$$

where *e* is exponent and determined coefficients are *a*=4,99·10^{-6} and *b*=-7,557.

As shown, partial desirability functions have the following form:

$$d_{PT} = \exp[-\exp(-1{,}994 + 2{,}470 \cdot I'_{PT})] \quad (5)$$

$$d_{RS} = \exp[-\exp(-1{,}720 + 0{,}0110 \cdot I'_{RS})] \quad (6)$$

$$d_{EX} = \exp[-\exp(-2{,}159 + 0{,}0132 \cdot I'_{EX})] \quad (7)$$

$$d_{TX} = \exp[-\exp(-2{,}159 + 0{,}0132 \cdot I'_{TX})] \quad (8)$$

The application of this approach characterizes obtained estimates of the hazard of a gas pipeline (for example) and summarized data are presented in Table. 2. The risk due to explosive hazard is at the limit of acceptable value with other optimistic indicators. Therefore, this area is subject to constant control over the provision of production conditions [6].

Table 2

Results of assessment of hazard and risk

Indicators of risk based on index estimates		Indicators of risk based on probabilistic estimates	
Name of the indicator	Value	A substantial component of risk	Value
Index of an accident	0,19	the occurrence of an accident due to exogenous and endogenous factors, outdated equipment, etc.	$1{,}096 \cdot 10^{-8}$
Index of Potential Damage	0,13	the occurrence of an accident from the maximum total amount of a hazardous substance of the same type, its threshold mass and the amount of such substances	$7{,}069 \cdot 10^{-9}$
Index of fire and explosion hazard	0,89	accident due to explosive substances, their quantity, the hazard of flare, thermal radiation	$2{,}191 \cdot 10^{-6}$
Relative Risk Index	0,09	possible negative consequences in the event of an accident at the enterprise, taking into account the worst case scenario	$4{,}937 \cdot 10^{-9}$
Regional Hazard Index	0,17	possible emergency situations due to features of the location of the facility (proximity to oil pipelines, railways, etc.).	$9{,}071 \cdot 10^{-9}$
Hazard category - low-risk facility		*The risk level is acceptable*	
The scale of hazard - object-oriented			

It should be noted that the system of indices is a measure of the criticality of an object stable mode. If the indices of regular work change, then the index values also change accordingly, and thus a probabilistic risk assessment.

While determining the indices for conditions of stable work we obtain the magnitude of the predicted level of risk, and for critical values of parameters - the value of the risk of the accident.

The developed methods have a modern program implementation.

Improvement of the regional development policy requires the involvement of long-term forecasting, ecological, economic, and sociological planning and strategic environmental assessment for the territorial planning system. Implementation of strategic environmental assessment in the planning process involves joint efforts to collect and analyze data, engage stakeholders and the public in order to effectively make decisions. Such joint activity is impossible without the continuous interaction of management, expert and interested parties, and therefore interaction should be built on the basis of a decision-oriented model.

Since the security of the regions is an integral part of sustainable development, the developed methodology is the basis for the development of implementation tools of strategic environmental assessment. For example, as a development indicator, an indicator of anthropogenic hazard is used $I_{TD} = \overline{\rho}_R \cdot J_{TD_\Sigma}$, $\overline{\rho}_R$ is the relative density of population in the region, J_{TD_Σ} is a generalized index of the technogenic hazard of the region, $J_{TD_\Sigma} = \sum_{i=1}^{n} J_{TD_i}$. The use of technogenic safety indicator will give a more complete picture of the sustainability level of individual territories and will provide an opportunity to see the actual level of man-made load.

Conclusion

This approach can be applied not only to existing industrial enterprises but also at the design stage in case of conducting a strategic environmental assessment or environmental impact assessment.The development of tools for implementing functions of strategic environmental assessment reduces uncertainty, increases the efficiency and adaptability of the decision-making cycle, facilitates access to information by experts, stakeholders and the public when conducting an environmental assessment of projects. The solution of these tasks contributes to the improvement of environmental legislation in the application of strategic environmental assessment as a compulsory instrument for strategic planning of socio-economic policy development at the national, regional and local levels, improvement of environmental protection, harmonization of economic, social and environmental development goals in regional strategies, plans, and programs.

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Assessment of Cyanobacteria Biomass Recourse Potential in Ukrainian Inland Waters for Environmentally Friendly Target Production

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Abstract* – *Assessment of perspective in using Ukrainian inland waters cyanobacteria biomass for multi-target production was conducted.

Keywords – biomass, cyanobacteria, environmental threat, biotechnology, resource potential.

Introduction

Searching for alternative energy sources under conditions of Ukrainian energy market alteration is specifically relevant. Among renewable energy sources that are used in world practice, prominent place takes biomass – wastes from wood processing, agricultural products, special forestry and agricultural energy plantings. In some regions, cultivating and using plants as a source for energy carriers production has been taken to such extent, that it led to reduction of agricultural production to a critical level and caused civil protests in some countries (Mexico, Latin America). This is why scientific efforts have been recently directed to search for cultivating technologies and applying it to energy producing biomass types, the use of which would not affect reduction of agricultural production potential opportunities and environmentally hazardous impact. Sets of studies (Israel – Seambiotic company, Japan – Gas and NEDO companies, USA - GreenFuel Technologies) have shown that algae can be the required biomass - both cultivated on special farms and harvested from hydrosphere surface objects. Such perspective for the Ukraine is cyanobacteria (blue-green algea) that have been recently causing environmental threats due to progressive water blooming. Water «blooming», dominant agents of which for Dnieper reservoirs are representatives of include *Microcystis, Phormidium, Aphanizomenon, Anabeana* and *Oscillatoria* genera, which are a biological signal of trouble in hydro-ecosystems. Among numerous mechanical, physical – chemical, biological and environmental methods for massive cyanobacteria development warning, the most effective are the last two, since they enable to avoid the cause, but not the consequences of water «blooming» [1]. Concerning perspectives for using them to obtain energy, then the most perspective solar energy utilizers appeared to be microalgae: maximum photosynthesis Energy conversion efficiency ratio gains 20%. Energy that is contained in 1 m^3 of biogass is equivalent to 0,6 m^3 of natural gas or 0,7 dm^3 of crude oil or 0,6 dm^3 of diesel fuel. That is why using cyanobacteria during their massive development (so called «blooming») in Dnieper reservoirs water area to obtain biogas will enable us to receive not only an additional energy source but will lead to improvement of sanitary-hygienic water level and coastal areas. Problem for such biogas production technology is cyanobacteria harvest, that can be carried out with the help of special barge-harvesters [2].

Additionally cyanobacteria biomass processing aiming to obtain products of different purpose can be relevant for such industry fields as medicine, pharmacology, cosmetology and parfume industry, as well as for agriculture (obtaining of organic-mineral fertilizers and organic pesticides) [3, 4].

Main part

In our opinion, in order to assess perspective biotechnologies of target products from Ukrainian internal water cyanobacteria biomass production, it is necessary to conduct range of complex studies. First of all, it is important to evaluate perspective of using cyanobacteria biomass resource potential for production of certain types of products: energy carriers, range of products from agricultural, medical, pharmacological, cosmetological and parfume industry. It is necessary to identify the most perspective types of cyanobacteria for application in each of these technologies and shape optimal application principles for these innovative technologies. It is worth to mention that for some products, essentially important are toxicological facilities of cyanobacteria. These facilities are also vital for minimization of environmental threats from uncontrolled development of cyanobacteria in Ukrainian inland water. And last but not least, it is important to study optimization and intensification of the harvest processes, concentration and preliminary processing of cyanobacteria in Ukrainian inland waters gaining its most effective application as resource potential in determined technologies that have been formerly studied.

As for perspectives from using resource potential of cyanobacteria to produce wide range of healthy products, then we previously suggested [3] scheme of biotechnological ways for complex processing of blue-green algae and fields for their application (Fig.1.)

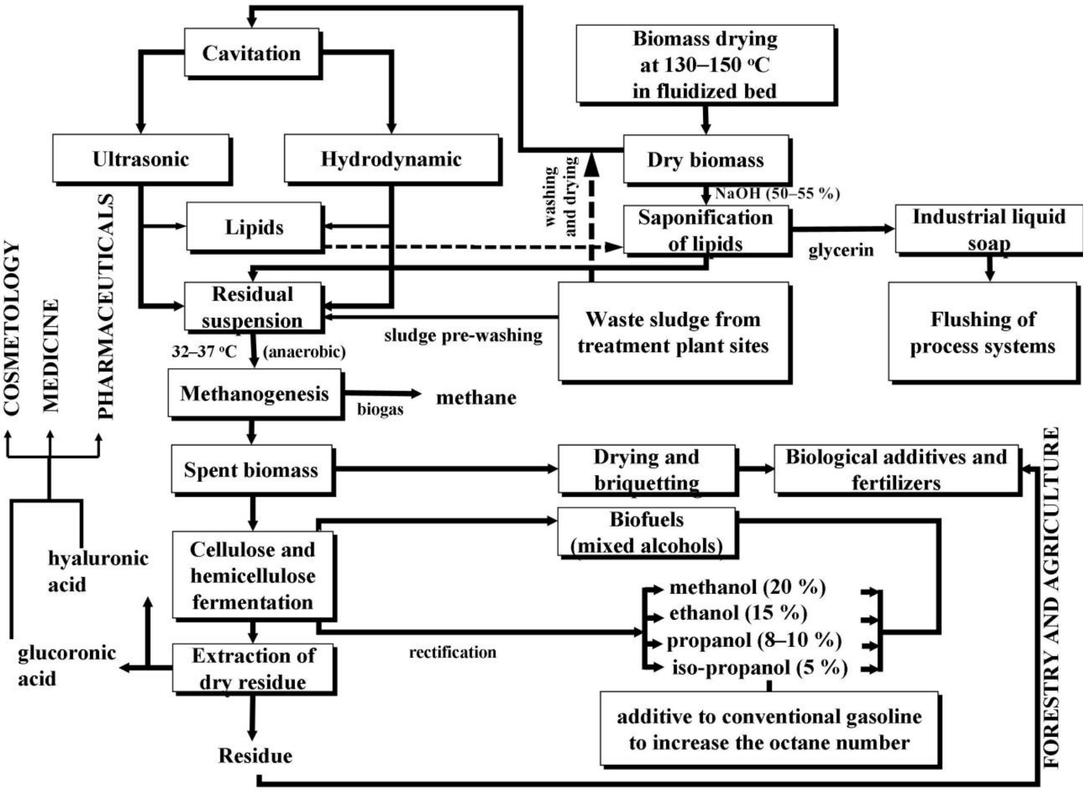

Fig.1. Biotechnological ways of blue-green algae complex processing and the industries of application of its products.

It has been fully studied for using cyanobacteria biomass as a resource potential in Ukrainian inland waters in energy carriers production technologies – implementation of methanogenesis technology with obtaining of condensed biogas [1,2,4] and lipid extraction with obtaining of raw material for biodiesel production [4]. It has been proven that the possibility of receiving condensed organic fertilizers from residual biomass after obtaining of biogas [4], previously conducted studies require generalization and concretization, necessary development of studies for establishing perspective in using cyanobacteria as organic pesticides.

Aspects in using cyanobacteria biomass as resource material in medicine, pharmacology, cosmetology and parfume industry require detailed studies. This is because this biomass is potential source of chromoproteids (comples of coloured proteins that change their colour depending on uptake), including phycobiliproteins (red and blue pigments). Hemeproteins, flavoproteins and phycobilins are also present in this biomass. Pigments that are added to cosmetic mixtures improve skin tissue breathing hence facilitate rejuvenation.

Hyaluronic and glucuronic acids are of special interests. Their synthesis under production conditions is very complicated, which is why cyanobacteria biomass is a valuable resource material for receiving these compounds. They are easily extracted from residual dry biomass via hydroalcohol extraction with further recrystallization under temperature above (40–50)°C. Under higher temperatures molecules of these multibasis organic acids lose biological activity since they become racemates or dycarboxylate.

Conclusion

Conducted analyses shows the perspectives of using cyanobacteria biomass of resource material for production of a variety products that are valuable in many industry fields and agriculture. What is important is that using this biomass as raw material, it is possible simultaneously to reduce the environmental threat from uncontrolled development of cyanobacteria in water areas of Ukrainian inland waters. Suggested algorithm of studies concerning identification of the most perspective types of cyanobacteria to concrete innovative technologies for target production.

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A simple Environmental-Friendly Method for Disposing Toxic Chemical Wastes

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Abstract – We present two methods of silver reduction from toxic chemical wastes containing silver by-products to make their disposal less complex and more environmental-friendly. We demonstrate the simplicity and advantages of these methods, which could be applied to educational or industrial laboratory facilities.

Keywords – green waste disposal, silver refining process, glucose and copper reduction, argentometry.

Introduction

Several argentometry techniques such as the Volhard or Bohr method are commonly used in educational institutions and industrial laboratories. These methods create different types of silver by-products that are considered harmful and must be discarded using specific protocols. Removing silver from such chemical wastes can be beneficial for three reasons. First, the remaining waste will be less toxic and hence, more environmentally friendly. Second, the waste without silver will be less expensive to dispose. Third, the recycled silver can be reused in the laboratory for other experiments.

The objective of this presentation is two-fold. First, we present and compare two methods to extract silver from waste solutions through precipitation, reduction with glucose [1] and reduction with copper [2]. Second, we will show how through further processing (melting and electrolysis) we can extract pure silver, which can be used in other laboratory experiments.

Materials and Methods

We have used three types of chemical waste (samples A, B, C) and two reduction methods (with glucose and copper). Sample A was obtained from the remaining of a chemistry experiment at TAV College and contained chicken broth soup, sodium chloride (NaCl), silver nitrate ($AgNO_3$), potassium chromate (K_2CrO_4), and water. Sample B consisted of a mixture of silver chloride (AgCl) and sodium chloride in water and was obtained from a different chemistry experiment at TAV, while sample C contained silver nitrate dissolved in water. Due to the nature and composition of the samples, we used the reduction with glucose on samples A and B and reduction with copper on sample C.

Here, we briefly discuss the two reduction methods. The glucose reduction method started by adding considerable amount of NaCl to ensure the formation of silver chloride (AgCl) precipitate from the waste solutions (Eq. (1)). We then added sodium hydroxide (NaOH) to form silver oxide (Ag_2O) from the precipitate (Eq. (2)). The addition of glucose then reduced the silver oxide to silver powder (Eq. (3)). Further, the powder was washed several times and the liquid was absorbed with a specific pump.

$$AgNO_{3(aq)} + NaCl_{(aq)} \rightarrow AgCl_{(s)} + NaNO_{3(aq)} \qquad (1)$$

$$2AgCl_{(s)} + 2NaOH_{(aq)} \rightarrow Ag_2O_{(s)} + 2NaCl_{(aq)} + H_2O_{(l)} \qquad (2)$$

$$Ag_2O_{(s)} + 2NaCl_{(aq)} + H_2O_{(l)} + NaOH_{(aq)} + C_6H_{12}O_{6(aq)} \rightarrow 2Ag_{(s)} + C_6H_{11}O_7Na_{(aq)} + 2NaCl_{(aq)} + 2H_2O_{(l)} \qquad (3)$$

The complete chemical equation which describes this process is:

$$AgCl_{(s)} + 3NaOH_{(aq)} + C_6\,H_{12}\,O_{6(aq)} \rightarrow 2Ag_{(s)} + C_6H_{11}O_7Na_{(aq)} + 2NaCl_{(aq)} + 2H_2O_{(l)} \qquad (4)$$

The copper reduction method consisted of forming silver precipitate directly by submerging copper rods in the silver nitrate solution (sample C) as described by Eq. (5).

$$2\ AgNO_{3(aq)} + Cu_{(s)} \rightarrow 2\ Ag_{(s)} + Cu\ (NO_3)_{2(a} \qquad (5)$$

To ensure maximum silver recovery we used two indicators, 0.5 M KI and 5%-K_2CrO_4 (according to Mohr method), to detect the presence of unreacted silver. After extraction, we used electrolysis to purify the silver powder after melting it. For electrolysis, a mixture of distilled water and $AgNO_3$ was added in a stainless-steel bowl. The impure silver was placed in a mesh which was submerged in the electrolytic cell. Finally, the pure silver powder was collected and melted into silver pellets.

Figure 1 presents the extracted dried silver powder collected after reduction with copper (Fig. 1a), the melted silver (Fig. 1b), and purified silver (Fig. 1c). The purity of the silver pellets was confirmed by scraping them into small pieces and then applying a drop of nitric acid followed by a drop of potassium chromate, following [3].

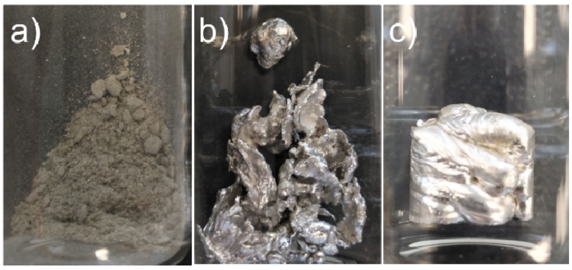

Fig.1 Dried silver powder extracted from copper reduction method (a), melted silver before purification (b), and purified silver (c).

Conclusion

We have shown the possibility of converting a toxic chemical waste into a less harmful solution, while recovering valuable material. The methods we presented can be reproduced in almost any laboratory environment and do not require extensive human or physical resources. The reduction with copper resulted in ~60% of silver recovery, while the glucose reduction yielded only ~15% silver recovery. Although, the reduction with copper seems less complex and more efficient, it is not possible to apply it on chemical wastes such as samples A and B, as the copper can unpredictably react with other chemicals present in the waste which lowers the possibility of silver precipitation.

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The Tandem Long-Term Program 2012-2021 and some Results on the Rehabilitation of Soil Biology of Intensively Farmed Agricultural Land in Germany

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Abstract* – *the used PHC preparations and current results of the monitoring biological soil parameters for the period 2006 to 2018 as well as results for the increase of yields with simultaneous reduced nitrogen use are presented.

Keywords – biological soil, photosynthesis, humus

Introduction

In recent decades, intensively used agricultural land in Germany has lost much of its natural soil fertility due to the use of extremely high levels of mineral nitrogen fertilizer and the intensive use of pesticides. Since 2005, we have been attempting to improve the biological soil fertility of these intensively used areas on about 170 agricultural areas with different soil indexes. The international long-term program Tandem$^{12/21}$ (2012-2021) and the two previous research projects Radostim A*B (2005-2008) and future$^{9/12}$ (2009-2012) have been investigating the potential of phytohormone-humic acid combinations (PHC) to increase soil biological fertility and to create a biological nutrient reserve in the soil.

In the spring, PHCs are applied during the growing season. They stimulate the photosynthesis of the plants and promote the development of soil biology. Since 2012, e.g. with the start of the tandem program, the same areas has also been undertaking an additional PHC application in the autumn in order to activate the conversion of the organic material to humus and to stabilize soil biology in the winter phase. In the following, the used PHC preparations and current results of the monitoring biological soil parameters for the period 2006 to 2018 as well as results for the increase of yields with simultaneous reduced nitrogen use are presented.

The PHC-preparation system (array) daRostim®TANDEM

The array daRostim®TANDEM has been used. It is free of chemically synthesized active ingredients and consists of 6 modifications, 3 for spring application (leaf application – F30, F50, F70) and 3 for autumn application (soil application – H30, H50, H70). By the modular selection of the composition of humic acids with a mass fraction of 50 to 85% of the organic substance and other plant-physiologically active components (natural plant hormone analogues, fatty acids, amino acids, polysaccharides) with a mass fraction of 0.01 to 0.07% of the organic substance, the modifications are optimally adapted to specific soil index (AZ). All 6 TANDEM modifications contain water with a mass fraction of about 90% as well as macro and micro elements. daRostim® TANDEM can be used in all field crops. The application is done with the sprayer, in the spring solo or together with the first phytosanitary measure, in the fall after harvest and before the winter sowing or intercrop essential parts of the ground (<30-40%) covered. The uniform dosage is 0.4 liters/ha [1].

Table 1.

The daRostim TANDEM Array

	Soil Index: 20 - 40	Soil Index: 20 - 40	Soil Index: 20 - 40
Leaf application (spring)	F30	F50	F70
Soil application (autumn)	H30	H50	H70

Monitoring of biological soil-parameters

Twice a year - at the end of March and at the end of October - soil samples are taken from a depth of 0 to 30cm and examined for the parameters humus, air-nitrogen fixing bacteria and phosphor-mobilizing bacteria. Figures 1 to 3 show the dynamics of these three parameters over a 12-year period:

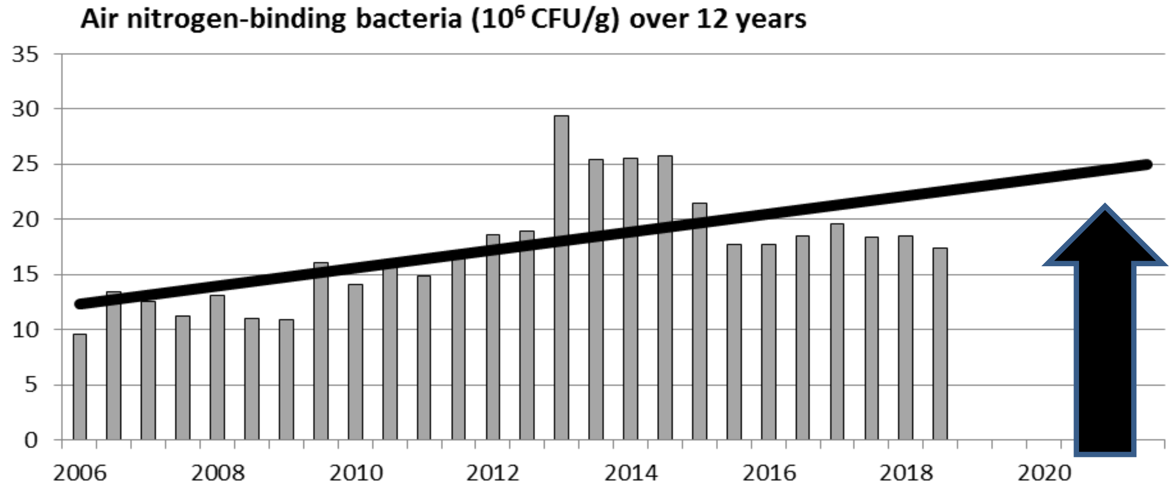

Fig. 1.

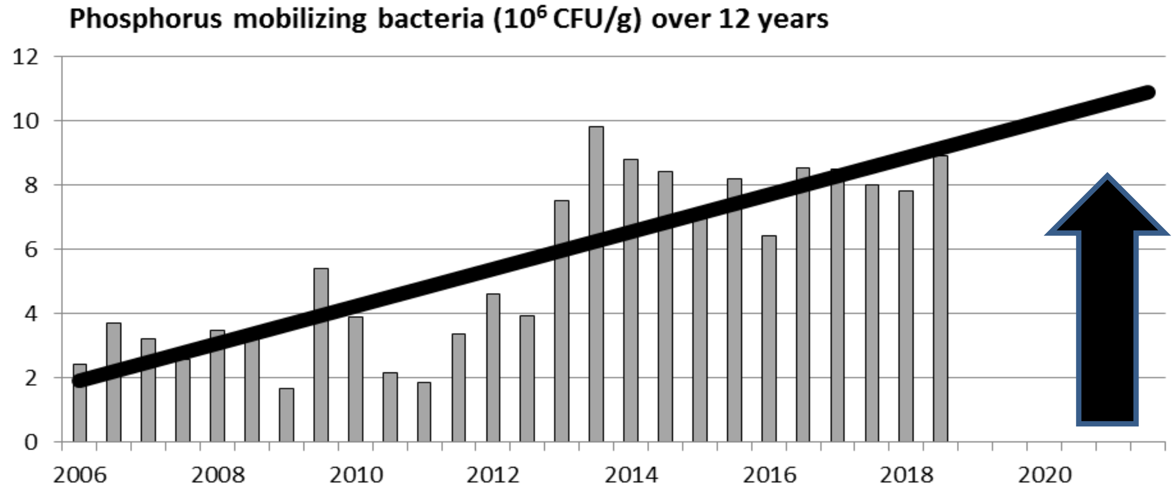

Fig. 2

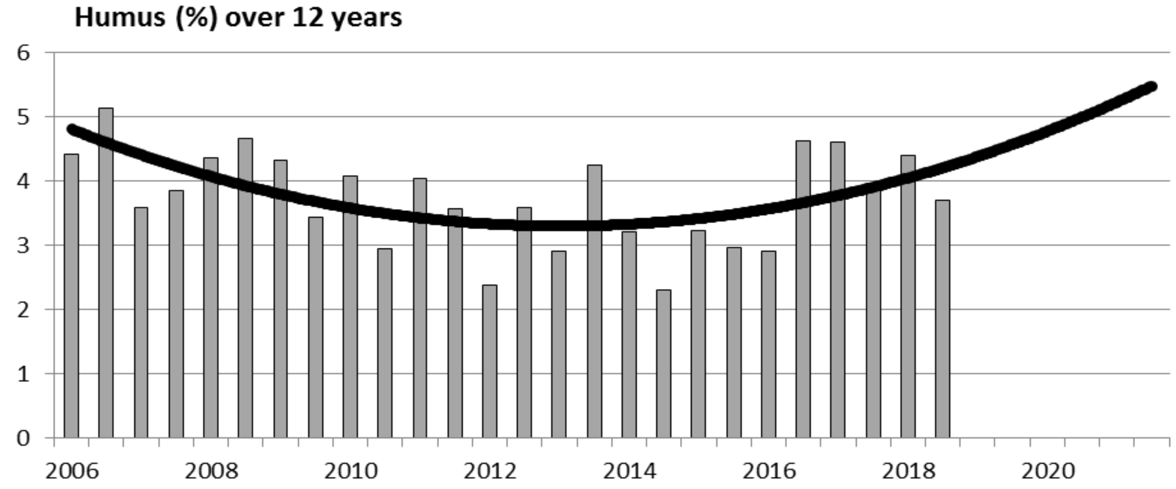

Fig. 3

Results and discussion

The particular specific effectiveness of daRostim®TANDEM is based on the combinatorial effect of phytohormones and humic acids (2nd generation PHC tandem technology). According to our findings, it is mainly the phytohormone component in the PHC that makes it possible to obtain the genetic to maximize the yield potential of a variety optimally. Phytohormones control and regulate the growth of plants in all stages of development, e.g. in germination, growth, seed maturity, flower formation or leaf fall. They are the messenger substances that circulate between the plant tissue, transport information and trigger specific reactions. In a complex interaction, they also help the plant to adapt to changing environmental conditions (drought, temperature, soil pH) and to form its own antibodies against phytopathogenic microorganisms. Primarily, the applied PHC increase photosynthetic performance by helping to produce more and faster chlorophyll and form larger leaf areas. The total amount of assimilates produced per unit time increases and this "more" is used in a secondary regulatory effect depending on the growth phase, the climatic factors and the metabolic situation in the root area (nutrient availability, water) of the plant for optimal reproduction, so the yield. The soil bacteria also benefit from this assimilate redistribution. The mean concentration of air nitrogen-binding bacteria increased by two times in 12 years on the 170 trial areas from 11 million CFU/g (2006) to 22 million CFU/g (2018), and for phosphor-mobilizing bacteria by six times from 1.5 million CFU/g to 9.0 Million CFU/g. By the additional PHC application in autumn increased the biological soil index BSI *, calculated from the relationship BSI * = 23/100 * (N + P) + H [2], by 25% (see Figure 4 and 5).

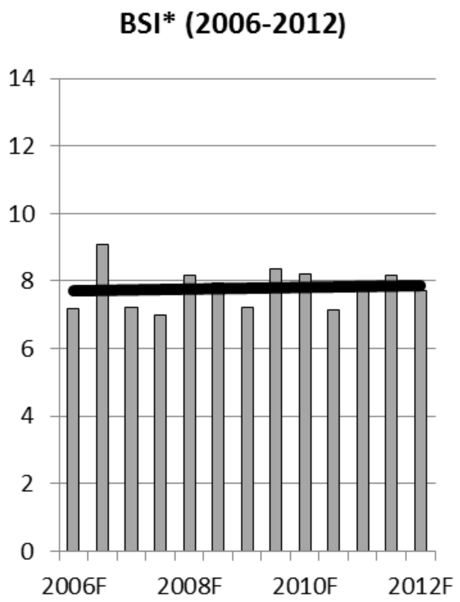

Fig. 4

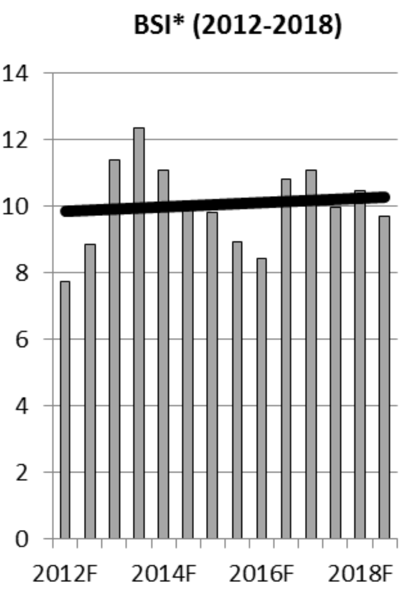

Fig. 5

With the "more" of air nitrogen-binding soil bacteria, the working point of the biological-nitrogen part of yield in the YEN-chart shifts towards higher yields with less nitrogen fertilizer use, the production functions shift in sync. As a result of the additional activation of soil biology by the PHC preparations, under the conditions of intensive cultivation in Germany on the 170 experimental areas an average yield increase of 13.7 CE was already established in 2016 with a simultaneous reduction of nitrogen fertilizer use by 26.2 kgN / ha. However, not all soils benefit equally well. The larger the soil index, the greater the average effect. This suggests that black soil with a soil index of 100, which provides the best natural conditions for the development of soil biology, could be particularly efficiently rehabilitated by PHC applications. Practical sector or yield increase and nitrogen fertilizer reduction vs soil index sector show Figure 6 and 7.

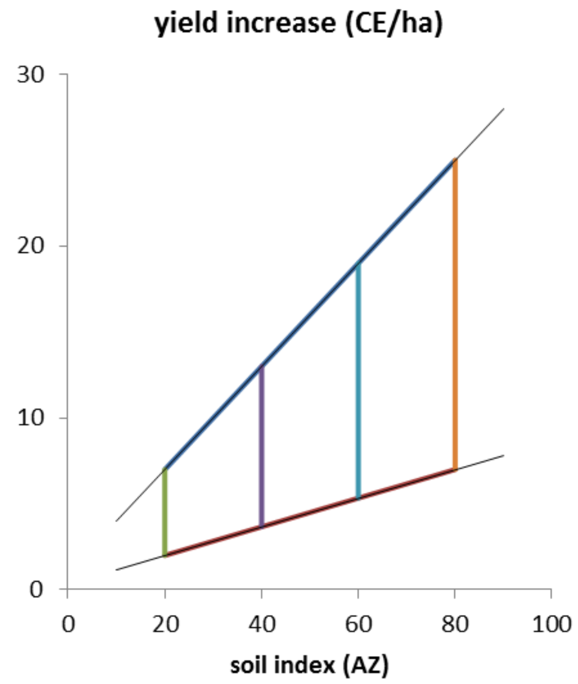

Fig. 6

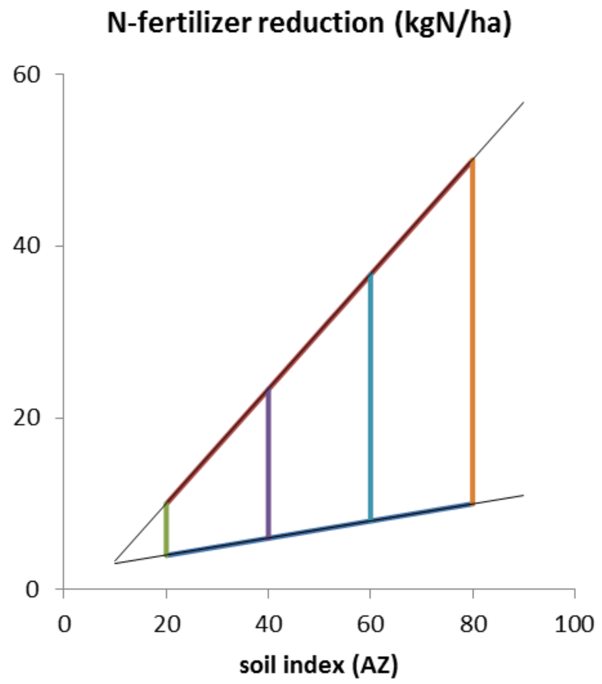

Fig. 7

The monetary effect from fertilizer saving and yield increase is very sustainable: 1 EUR PHC use beats conservatively (0.6 EUR/kg N, 10 EUR/CE) with 2 to 6 EUR profit. Our results are shown in Table 2.

Table 2.

Monetary effect of TANDEM-Application

PHC- Effect (EUR/ha)	Soil index		
	20 - 40	40 - 60	60 - 80
Economic yield	51,30	179,90	239,70
Total cost of preparations used in thw applications (F+H)	21,60	31,20	41,04
benefit /cost - ratio	**2,38**	**5,77**	**5,84**

Expression of thanks

The author thanks the companies in Bückwitz, Borna, Cavertitz, Doberschütz, Dittmannsdorf, Elsterberg, Gimmel, Großräschen, Görzig, Großthiemig, Hohenroda, Herzogswalde, Lauenhain, Münchenbernsdorf, Pahren, Reichenbach, Sprotta, Uftrungen und Wülknitz for their many years of stable cooperation.

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Polyacrylamide Application for Dewatering of Clay Slimes From Halurgy Plants by Centrifugation

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Abstract – The influence of precipitation centrifugation on the dewatering efficiency of clay-salt sludges. The moisture content of the resulting sludge was found to be decreased in proportion to the increase of the centrifuge separation factor. The addition of polyacrylamide solution to the suspension allows to reduce the moisture content of centrifuged sludge by 3...4%.

Keywords: clay sludge, precipitation centrifugation, polyacrylamide, humidity.

Introduction

Polymineral potassium ores of the Precarpathian region, Ukraine, are characterized by a high content of clay impurities, which reaches 20...25% by weight. Ores processing is accompanied by the formation of clay-salt sludges, with which the useful ore components are lost. The existing technology includes three-stage washing of sludge with settling, which is ineffective and complicates the technological process. The washed sludge has high humidity and salt content. To intensify the process and minimize the content of washing solution in the final sludge, it is advisable to apply a centrifugation method.

Experimental part

Polymineral potassium ore (Stebnitsky deposit, Ukraine) with 12.3% of clay impurities was used in this research. It was dissolved in water and saturated solution was separated with decanting of clay sludge. The sludge was homogenized and centrifuged on laboratory centrifuges of precipitating type. The influence of the centrifuge separation factor (in the range of 1160 ... 8700) and the centrifugation time on the moisture content was investigated in a centrifuged precipitate. To intensify the precipitation 0.25% solution of polyacrylamide was added as a flocculant. The experiments were carried out both with and without it. The moisture content in the sludge was determined by its drying at 105...110 ° C till the weight became constant. The centrifugation efficiency was evaluated relative to the moisture content in the final sludge (wt. %).

The research results showed that at the same centrifugation time (5 minutes), the moisture content of centrifuged sludges varied from 33 to 28% with an increase in the separation factor in the investigated range according to the dependence close to the proportional one. After the flocculant addition to the suspension, some aggregation of clay particles occurred, resulting in the decrease of centrifuged sludge moisture content by 3...4% compared with the previous experiments. At the same time, the higher the separation factor, the more significant reduction. Recentrifugation of the sludge provided the reduction of moisture content by another 3%, indicating the ability of the sludge to be compressed.

Conclusions

For the dewatering of clay sludge from halurgy plants, it is advisable to use the precipitation centrifugation method, which makes it possible to intensify and simplify the technology. Adding the polyacrylamide to the initial suspension helps to reduce the final moisture content by 3...4%.

Improvement of Technology of Bioenergetic Raw Material by Cavitational Homogenization of River Blue-Green Water Plants

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Abstract* – The improved technological scheme of fermentational processing blue-greenwater plants into biogas includes three main blocks is proposed. The block of accumulating and preparation of water suspension of blue-green water plants, the block of preparation of the biomass of blue-green water plants by homogenization with vibro activators and the block of biogas fermentation by the process of "methane fermentation" includes. As a result the output of the ready product, biogas from 1 ton ofblue-green water plants bio-mass is about 30 m^3, which equals 0.6 tons of oil or 0.51 tons of diesel fuel.

Keywords – blue-green water plants, vibroresonance cavitation, technological scheme, homogenization.

Introduction

One of the most active pollutants of fresh water on the territory of Ukraine is diverse species of the so-called Cyanobacteria, named blue-green water plants. On our territory there are about ten species, the most widely- spread, according to Parker System of Water Plants, belong to Procaryota kingdom, to Cianophycota class, to Cianophyceae family. During its vegetation period (70-120 days) one initial cell of cyanobacterium can produce 10^{20} ones, this fact accounts for their massive development, known as "flowering of water" [1]. The volume of water infected by cyanobacteria and, consequently, the number of cyanobacteria in waters of Ukraine is enormous. According to this research, carried out only on Kremenchuk reservoir with the area of water mirror 2250 square kilometers and volume of 828 billion cubic meters of shallow water at average thickness of water saturation by cyanobacteria 50 kilo/m^3, then general biomass equals $4.14*10^7$ tons of accumulations during the whole summer vegetation period [2]. Water polluted by cyanobacteria not only deteriorates ecology of reservoirs and environment, but also becomes unfit and dangerous for people and animals, because of possible poisoning as a result of using it.

Description

The aim of the research is improvement of technology of blue-green water plants processing into bio-gas by their cavitational homogenization.

Cavitational processing of water suspension of blue-green water plants due to appearing cavitational microbulbs of striking micro waves while splashing, in turn changing zones of high and low pressure, as well as intensive influence of self created in cavitational field chemically active oxidizers radicals OH^- and hydrogen peroxide H_2O_2 on membranes and covers of water plants, actively ruins covers of water plants and frees their cell contents. This way is defended by a patent for a useful model of Ukraine and provides using hydrodynamic cavitation on the stage of "extraction and bio-decomposition" [2]. It accelerates the speed of ruining covers of cyanobacteria by 20-25%.

To accelerate the effectiveness of blue-greenwater plants cavitational homogenization an improved construction of a vibroresonance vibroactivator is proposed [3]. The essence of the improvement is that agitators of cavitation are installed opposite each other on the fluctuating and fixed on the frames of starters; the outer surface of them has the shape of hyperboloid of rotation, and the side surface has the shape of drawn into the hyperboloid hemisphere with a radius equal to double scope of working camera oscillation.

Based on experimental research data of vibroresonance cavitational processing of blue-green water plants suspension taking plant suspension taking into consideration constructive opportunities and characteristic features of the elaborated construction of an industrial vibroactivator, an improved principal technological scheme of the process of processing of blue-green water plants into biogas is proposed. This scheme includes three main blocks, namely: I block is a block of accumulating raw material and preparation of water suspension of blue-greenwater plants; II block is a block of vibroresonanse homogenization of water plant suspension; and III block is a block of bio-gas fermentation by anaerobic methane fermentation.

The difference of the proposed technological process of processing blue-green plants into biogas from typically traditional is supplementary installation of cavitational installation of cavitational homogenization of biomass in this block. As a result the output of the product, biogas, is about 30 m^3 from 1 ton for biomass of blue-green plants which equals in thermal capacity of burning 0.6 tons of oil or 0.51 tons of diesel fuel.

Conclusion

1. The results of this research are applicable to two important aspects of mankind. Firstly, it is improvement of environmental ecology due to annihilation of active pollutants of natural water, cyanobacteria. Secondly, a very important sphere of energetics, bioenergetics, is improved; it is based on using renewable sources of energy, blue-green water plants.

2. Homogenization of blue-green suspension with equipment of vibroresonance cavitation raised volumes of fermentation by 25-30% from their biomass of biogas. This is 10-15% higher level comparing to homogenization of water plant biomass by hydrodynamic cavitational processing with paddle cavitators, and exceeds volumes of fermentation after ultrasound processing by 15-20%.

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Alternative Methods for Replacing Propellants in the Medical Form "Spray"

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Abstract* – *Recently, the range of medicines is expanding its nomenclature more and more with medicines and medical products in the form of pressure spray. We decided to analyze the Ukrainian market for the presence of ozone-depleting components - propellants in this dosage form. Since this problem was relevant, the possibility of using the modern packaging system was analyzed.

Keywords – nasal spray, propellant, ozone layer, packaging system, chladone.

Introduction

Sprays are solutions, emulsions or suspensions, they are intended for local application on the skin, mucous membranes or for inhalations. Important for the delivery of the product from the container are scattering or evacuation gases, through which the inside of the containers creates pressure. These gases are called propellants. Propellants are classified by the size of the pressure of saturated vapors, at aggregate state under normal conditions and by chemical nature.

The results and discussion

Literary sources indicate, that in drugs under pressure, liquefied gases - chladones - are most commonly used. It is known that chladones adversely affect the protective ozone layer of the Earth. The high chemical stability of the chladones creates the possibility of their gradual accumulation in the troposphere and the achievement of the Earth's ozone layer [1]. After analyzing the pharmaceutical market, we realized that spray and aerosol production still had harmful spells, which led us to find alternative and advantageous replacement manufacturers. Table 1 presents pharmaceutical products of the Ukrainian pharmaceutical market, containing chladones [2].

Table 1

List of drugs containing chladones as propellant

Name of the drug	Medical form	Propellant	Manufacturer
Hepiderm forte	Spume on the skin	Chladon 134a	«Zdorovya»
Hepiderm health forte	Spume on the skin	Chladon 134a	«Zdorovya»

Since the abandonment of harmful propellants is essential, we have decided to describe the cheapest and most modern way of releasing liquid from the packaging.

This is a study on the replacement of ozone-depleting substances in aerosols by mechanical valves-dispersal systems: mechanical pumps, compression cylinders and barrier partitions. The advantages of such packages are full explosion safety, reusability of use, the possibility of more effective use of the internal volume of the bottle [1].

Using a mechanical pump, the output of the bottle content is by compressed air. With the aid of a micropump, the air pressure inside is increased to 5 atm, which provides the exact dose of drugs and homogeneity of their dosage. These parameters make this type of packaging alternative of any propellent product.

In addition to mechanical pumps, compression cylinders are used which are made of elastic polymers. The principle of their work is based on the actions of the muscular force of compression and squeezing the product through a nozzle with a small section. Such packages are the cheapest, since they do not require the cost of other component packages.

The above-mentioned containers have one common drawback - the inability to achieve sufficient internal pressure, comparable to the pressure created by conventional containers with liquefied propellants [1].

In view of this, we have reviewed the most advanced packaging options for sprays. Nowadays, a new packaging, known as "barrier", has become widespread. Its essence lies in the fact that the product is separated from the propellant by a movable partition, which prevents the contact between them - the chemical interaction between the propellant and the product, as well as the flow of propellant into the atmosphere, is excluded. Structurally two-chamber packages are executed in different variants: with a piston, with an insert, with an inner bag (more commonly known as Bag-On-Valve technology) [1]. Figure 1 shows that the BOV system, as a modern packaging system, is an alternative and promising, since many manufacturers already use this type of packaging.

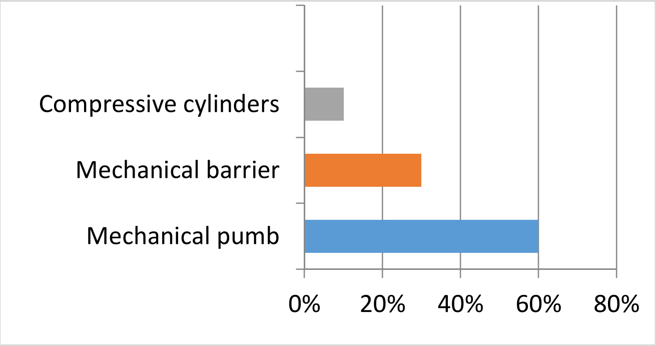

Fig.1. Availability of mechanical packaging systems in the pharmaceutical market of Ukraine

Conclusion

The using of new formulations of drugs and modern equipment allows the introduction of environmentally safe packaging systems for pharmaceutical sprays and aerosols, thereby significantly reducing the detrimental effects of propellants on the ozone layer of the Earth. In contrast to the use of propellant in production, we proposed to pay attention to the transition of manufacturers to the modern packaging system, or to separate the propellant from the product mechanically, thus preventing the penetration of the propellant into the atmosphere.

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Preparation of Bitumen Using Acidic Tars

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Abstract* – The studies undertaken have established the effect of the ratio of acid tar coupled with straight-run petroleum tars introduced into the process. The influence temperature of the process, of final heating temperature of the bitumen mass in the reactor and of stirring intensity of the reaction mixture in the reactor on the quality is installed.

Keywords - acid tar, asphalt, bitumen, ductility, penetration

Introduction

Acid tar (AT) belong to the II class hazard waste. To date, there are no universal technologies for their complex processing. This creates serious difficulties in the disposal of storage ponds AT. The acid tars are wastes from oil refining and petrochemical industries that are troublesome for disposal. They are formed during purification of special oils such as condenser, transformer, hydraulic, medical, perfumery oil, etc., as well as in production of flotation reagents and additives, in sulfonation of individual hydrocarbons and petroleum fractions. [1, 2]. AT are occupy the second place in the accumulation after oil sludge. According to the physico-chemical composition - it is a gum-like tall bulk mass containing various organic compounds, sulfuric acid and water.

Acid tars are pose an environmental hazard in that their chemical composition does not actually allow direct consumption, because that acid tars are dumped in gathering ponds, as results, is have create a significant environmental hazard without proper utilization. With such methods used for ATs disposal, environmental pollution occurs, leading to acidification of soil and water bodies, and, consequently, to destruction of flora and fauna. A natural continuous oxidation-reduction process causes the release of a large amount of sulfur dioxide, which, in turn, contaminates the air basin. The acid tar ponds are prompted on vast areas thens contain thousands of tons of wastes with the total mass in Ukraine and abroad reaching millions of tons. Thus, only on the territory of Lviv region not less than 150 thousand m^3 of acid tars are found [3, 6].

Over a long period of use in the petroleum industry method of cleaning oil sulfuric acid recycling is propose realizing in many options that create acidic tars. This is because the acid tars, as already mentioned, are dangerous to the environment and pose significant environmental problems. Also, in the tanks of acid dusts, a large amount of hydrocarbons and other compounds are concentrated, which, of course, must be utilized for industrial use [4]. Modern technologies for ATs disposal according to the influence on wastes are as follows:

- pyrolysis under the influence of high temperatures (800 – 1200 °C) producing H_2SO_4, heat, high-sulfur coke, activated carbon [5];
- low temperature decomposition within 150 – 350 °C followed by bitumen generation [6];
- water or steam hydrolysis producing dilute H_2SO_4 and fuel components;

- neutralization by various agents with the receipt of fuel, surfactants, or for waste disposal [7].

Experimental

The purpose of the study was to identify the influence of various parameters on treatment of acid tar that has been dumped in lagoons for a long time by turning it into petroleum-based bitumen [8].

To achieve a target goal, the following tasks were solved:

– to determine the influence on the qualitative characteristics of bitumen and smoothness of the process, that is, the ratio of acid tar to straight-run tar taken into the process; temperature of the process; specific feed rate of acid tar to the reactor; rate of temperature rise in the reactor; final heating temperature of the bituminous mass in the reactor and the intensity at which the reaction mixture is mixed in the reactor;

– to establish optimal conditions for acid tar treatment with conversion to petroleum-based bitumen.

The bituminous mass is generated from a mixture of acid and straight-run tars when they are simultaneously heated. At the same time oxidation occurs with sulfuric acid as the organic mass at elevated temperatures appears to be a reducing medium for sulfuric acid. The resulting sulphuric anhydride oxidizes an organic matter, turning it into bituminous mass. The quality and yield of bitumen and the smoothness of the process can be affected by a significant number factors.

The following main parameters of the properties of obtained bitumens were ductility, penetration, softening point and solubility in an organic solvent (benzene).

Studies have indicated that with increasing content in the mixture of acidic tar, the softening temperature increases, while the ductility and penetration decreases.

The study showed that the initial temperature in the reactor core has little effect on bitumen quality indicators: softening temperature, ductility, penetration, solubility in benzene content of water-soluble compounds, acids and alkalis. However, the initial temperature in the reactor affects the flow of the process. As the temperature in the reactor rises above 160 °C, increased foam generation together with a marked increase in the reaction mass is observed. So when acid tars is fed to straight-run tar that is heated above 100 °C, the reaction of sulfuric acid with the most reactive components of tar initiates. The acid tar feed to the reactor at a temperature above 200 °C serves to obtain the bitumen in which the homogeneity is disturbed and available consolidating products are in the form of small grains. Studies have shown that the specific feed rate of acid tar to the reactor has no decisive impact on the quality of the resulting bitumen. Increasing specific feed rate of acid tar causes process intensification, an increase in gas release and foam formation.

According to the study, the process of obtaining bitumen from a mixture of acid and straight-run tars can be performed when they are mixed on one occasion by the temperature of the mixture that should be lower than 100 °C. It should be noted that the next mixture heating has to be at the rate of temperature rise within 1.5 – 2 °C/min, then vapor liberation and foam generation are found to be less intense, and the reaction volume is increased only by 2-3 times.

It is to be admitted, however, that straight and acid tars are substances of high viscosity, and, therefore, the intensity of mass transfer will significantly affect the intensity and smoothness of the process. So then, mixing is an obligatory condition to conduct the process. Mixing intensity that underwent examination in the range of 50 to 250 turns per minute showed no such effect on the quality of the obtained bitumens at equal initial conditions. The results suggest the following: if not mixed a low-quality heterogeneous bituminous mass is produced; and asphaltenes that are formed due to high molecular weight and high adhesion are precipitated on the walls of the reactor. As a result, with exposure to high temperature, asphaltenes are carbonized being turned into a low-soluble product that impedes the heating of the entire reaction mass. On the other hand, the mixing process enables not only to avoid precipitation of asphaltenes but also reduces the foam formation and the volume of the reaction mass.

The technological features of using acid tar in the bitumen production have been examined and the optimal conditions of the process have been established, such as the acid tar content is 20 – 35 % in the mixture, final heating temperature of the bituminous mass is equal to 300-320 °C, the specific feed rate of acid tar in the mixture amounts to 2.5 – 6 g/(min×kg), the rate of temperature rise in the reactor is represented by 2–5 °C/min. The first two factors have a significant effect on the quality of bitumens, while others on the smoothness of the process.

Conclusion

The results of the research suggest the following: poor quality is obtained without mixing heterogeneous mass bitumen and asphaltenes formed as a result of high molecular weight and high adgesion are deposited on the walls of the reactor. As a result, asphaltenes are exposed to high temperature and carbolization, becoming insoluble product that prevents heating of the entire mass. However, mixing allows not only to avoid sedimentation of asphaltenes, but also reduces foaming reaction mass and volume.

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Scorpionates: Coordination Chemistry Comes Home

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***Abstract* – Some underreported aspects of polypyrazolylborate chemistry are explored, in particular novel lanthanide coordination chemistry and zwitterionic ligand replacements of this so-called "scorpionate" class of ligands. The application of these ligands to future materials engineering is postulated and, finally, the historic relevance of the topic to L'viv is described.**

Keywords – scorpionates, scorpionate ligands, polypyrazolylborates, polypyrazolylborate ligands, Trofimenko, Swiatoslaw, materials engineering, lanthanide ions.

Introduction

Since their reporting [1] by Swiatoslaw Trofimenko in 1967 the polypyrazolylborate, or 'scorpionate', class of ligands (Tp^-, Figure 1) has been used to form complexes with a wide variety of metals around the periodic table [2].

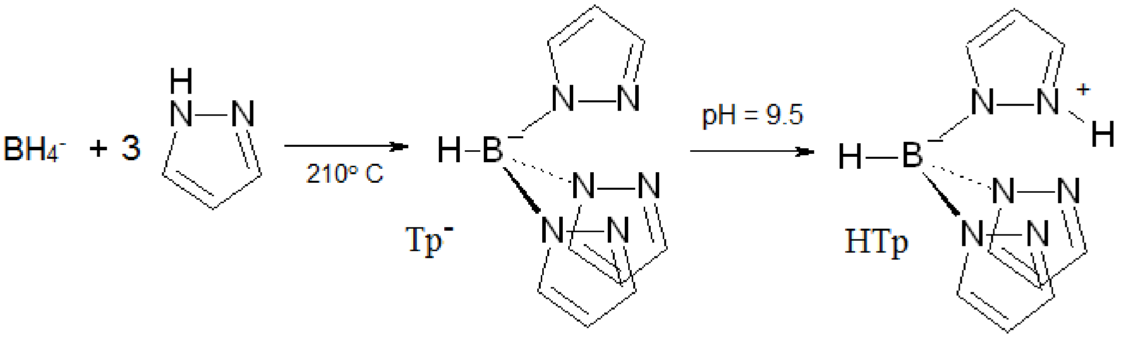

Fig. 1: Synthesis of Tp- and HTp

The trivalent lanthanide metal ions possess unique and desirable properties such as high magnetism or luminescence which might be incorporated into polymeric ‘plastics’ to afford cheaply shaped, but highly specialised, materials. We were interested in the idea of fixing one lanthanide ion proximally to one double bond in the hope that the resulting materials might be amenable to reproducible copolymerisation to afford a reasonably homogeneous copolymer, locating Ln centres at predictably-distant ‘island’ points in any product, wherefrom they might migrate only under great stress. Our interest in scorpionate chemistry is reinforced by the observation that a stable family of lanthanide acetate complexes [$LnTp_2(OOCCH_3)$] can be produced for the whole of the lanthanide series (Ln = La-Lu) [3]. Our hope is that the substitution of the acetate ligand for one containing C=C double bonds might allow the incorporation of {$LnTp_2$} moieties, along with the desirable associated properties of Ln ions, into highly processible materials such as polymers, by co-polymerisation.

A second point of our interest in the scorpionate ligands is concerned with the synthesis of scorpionate complexes with d-block metals, immediately from other labile complexes, by direct use of the free acid HTp [1], Figure 1. This moderately stable and presumably zwitterionic species can act as a protonating agent for formally anionic ligands [4] and, concomitantly, as a chelating agent displacing existing neutral ligands from the metal coordination sphere. This under-explored class of reagents can afford, in labile complexes, the transformation of complexes containing one class of ligands, directly to those containing the Tp ligand.

Lanthanide Coordination Chemistry Studies

Titration of a 2:1 mixture of aqueous Tp$^-$:crot$^-$ into stirred aqueous solutions of lanthanide chlorides or nitrates afforded complexes of the expected [LnTp$_2$(crot)] (crot$^-$ = $CH_3CH{=}CHCOO^-$) formulation for the later lanthanides (Ho-Lu), confirmed by a single-crystal X-ray study of the Ho complex (Figure 2).

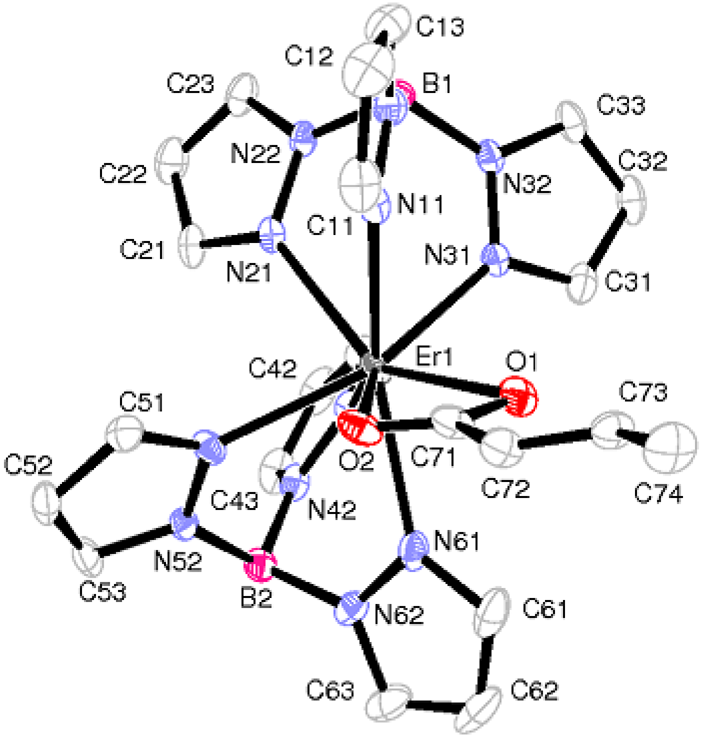

Fig. 2. The single-crystal X-ray structure of [HoTp$_2$(crot)]

However, it was clear from spectroscopic data that we had formed complexes falling into two morphological families, whose infrared properties are summarised in Table 1.

Table 1:

Selected infrared spectral data for lanthanide crotonate complexes

	υ(BH)	υ(CO)		υ(BH)	υ(CO)
La	-	-	?[DyTp(crot)$_2$]$_2$	2453/2494	1657
[CeTp(crot)$_2$]$_2$	2451	1661	[HoTp(crot)$_2$]$_2$[a]	2494	1656
[PrTp(crot)$_2$]$_2$	2452	1660	[HoTp$_2$(crot)][b]	2474	1655
[NdTp(crot)$_2$]$_2$	2442	1660	?[ErTp$_2$(crot)]	2458/2447	1665
[SmTp(crot)$_2$]$_2$	2447	1657	[TmTp$_2$(crot)]	2475	1655
[EuTp(crot)$_2$]$_2$	2450	1657	[YbTp$_2$(crot)]	2475	1655
[GdTp(crot)$_2$]$_2$	2451	1658	[LuTp$_2$(crot)]	2475	1656
[TbTp(crot)$_2$]$_2$	2452	1659			
[a] Tornote block crystals, crystallising first. [b] Globlar clumps, crystallising last.					

The earlier, larger lanthanide ions adopt a novel structural type [LnTp(crot)$_2$]$_2$ incorporating unusual (μ_2-κ^2,κ^1) bridging crotonate ligands, affording the metal ions 8-coordination (Figure 3).

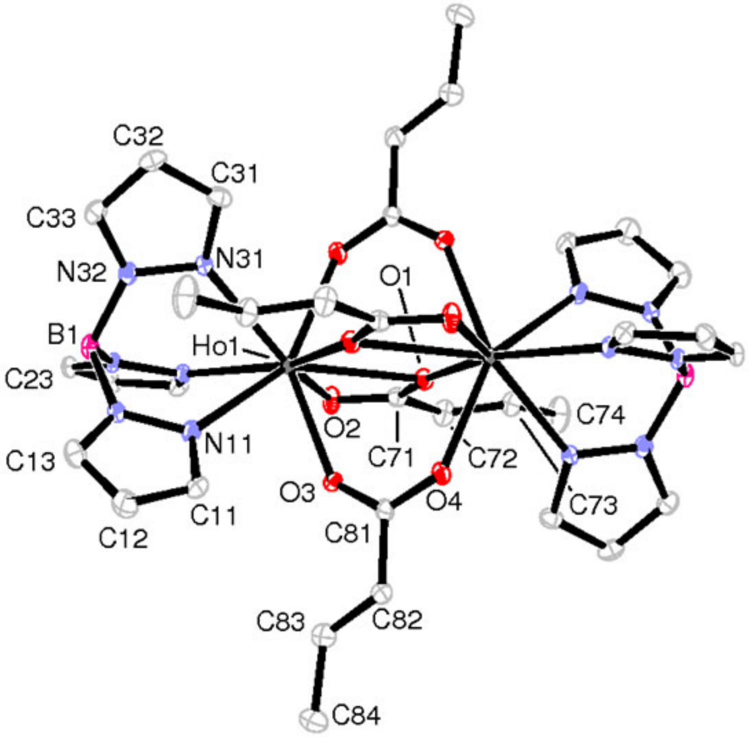

Fig. 3. The single-crystal X-ray structure of $[HoTp(crot)_2]_2$

Clearly either complex type might be potentially suitable for co-polymerisation, and we have also obtained potentially useful analogous cinnamate complexes for future study.

Free Acid Studies

The free acid HTp, like the free acids of all other polypyrazolylborates, is of only moderate stability, decomposing over a few days [1]. However, it does have a surprisingly low melting point of about 95 °C, allowing it to be molten together with its potential co-reagent. In this way a variety of ligand replacement reactions may be carried out, as shown in Figure 4.

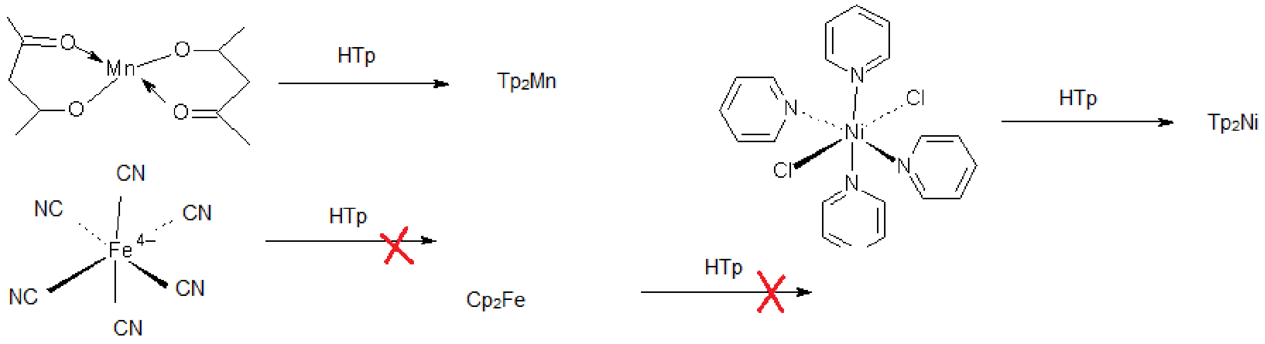

Fig. 4. Typical reactions of the free acid HTp

The concept of the reactions proceeding by ligand protonation, followed by replacement of ligands by Tp seemed a straightforward one – for example the reaction Cp_2ZrCl_2 + HTp --> $TpCpZrCl_2$ + HCp ($Cp^- = C_5H_5^-$) was accompanied by the aroma of cyclopentadiene. However, no amount of HTp, moderate or excess [5], when reacted with Cp_2ZrCl_2, would afford Tp_2ZrCl_2. Instead, ill-characterised Zr species, possibly $TpZrCl_3$ derivatives, were isolated as well as 1,4-bispyrazolylpyrazaboles (Figure 5), which are the breakdown products of HTp and whose relative proportions (1,4-*cis*- or 1,4-*trans*-) are dictated by the absence or presence of Cp_2ZrCl_2 [6].

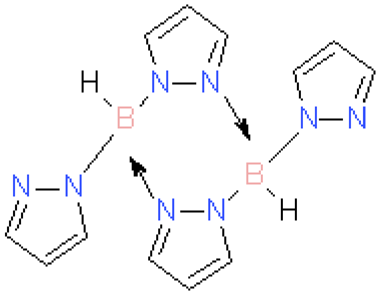

Figure 5. 1,4-bispyrazolylpyrazabole

Conclusion

The latter few sentences above conclude this brief account of polypyrazolylborate (or scorpionate) chemistry in an appropriate way, interrelating the three main advances introduced by Swiatoslaw Trofimenko in the mid-1960s. In two seminal papers in the mid-1960s he described the new polypyrazolylborate ligands [1], their novel free acids [1] and the new pyrazaboles [7]. The authors summarise only a few of their own observations, spanning four decades, interrelating the above original themes in novel ways. There is so much more.

Swiatoslaw 'Jerry' Trofimenko passed away in the USA on 26 February 2007, but he was born in Lviv in 1931. The authors are humbly grateful in 2019 to have the pleasure of describing some of their own investigations, of chemistry originating from Lviv, at the place of its 'origin'.

Acknowledgments

The authors wish to thank Prof. Jon McCleverty, Dr Chris Jones and Prof Peter Foot for past support. This short account is dedicated to the memory of Swiatoslaw Trofimenko.

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Metal forms in bottom sediments as a bioavailability indicator

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Abstract. This study assessed the risk of water biocenosis caused by the potentially bioavailable metal forms. In a simple extraction process, the efficiency of metals eluting from the sediments was highest for EDTA solution . Sequential extraction has confirmed the diverse bioavailability of metals in the aquatic environment.

Keywords: metals, sediments, single and sequential speciation, bioavailability

Introduction

Upon reaching water, metals react with substances contained in it, then settle on the bottom and react with the sediment components. The most important processes of metal immobilization in sediments are: chemisorption, precipitation, co-precipitation and complexation [1, 2]. In mineral structures, ion of K^+ or Ca^{2+} can be exchanged for other ion metals (Me^{2+}), e.g in clay or shells. Carbonates and phosphates are other important components in these processes. Chemisorption and co-precipitation of metals heavily depends on the presence of hydrated Fe/Mn oxides. These metals are chemically reactive in their reduced form of Fe(II) and Mn(II), and insoluble forms are present in the oxidized compounds Mn(III, IV), Fe(III). On the surface of these compounds sorption of hydrogen ions or of metal cations occurs as following [3]:

$$FeO(OH) + Me^{2+} \leftrightarrow FeO(OH)\text{-}M \leftrightarrow (FeO(O)\text{-}Me)^{+} + H^{+}$$

Karczewska [4] showed, that manganese oxides bind 1-30 % of total Cu content, 1-26 % of Pb, 4-27% of Zn and <1% of As, amorphous iron oxides bind 3-24% Cu, 1-54% Pb, 3-25% Zn and 42-90% As, and crystalline oxides: 3- 29% Cu, 1-53% Pb, 9-34% Zn and 5-46% As.

An equally important solid phase of metal binding in sediments are sulfides (eg. FeS), in which iron can be replaced with another metal, according to the equation:

$$Me^{2+} + FeS_{(s)} === MeS_{(s)} + Fe^{2+}$$

Metals bound in sulfides can be released under appropriate conditions into an aqueous solution.

The high contribution of Cd in mobile sediment forms may be due to the process in which cadmium sulfide is partially or completely oxidized to a soluble form of $CdSO_4$ under aerobic conditions:

$$CdS\ (s) + 2O_2 == Cd^{2+} + SO_4^{2-}$$

This reaction is very likely to happen in the shallow river sediments, where near-bottom layers of the river are well oxygenated and where variable hydrological conditions along with redox potential changes at the water- sediment boundary can be observed.

The chemical composition of bottom sediments is in many cases a better environmental pollution indicator than the water composition. The content of chemical elements changes between the sediment layers, showing the historical contamination changes of the reservoir [5].

In environmental studies of bottom sediment samples, the total metal content is the most popular indicator, because it shows the extent of sediment contamination. Bioavailability and mobility may be assessed by using a single (simple) extraction, where the natural conditions of components passing from the testing sample directly to the solution are simulated [6]. The single extraction method consists of applying the extrahent to the sediment sample to determine the metal forms, which then pass to the extraction solution. It reflects the biological metal bioavailability by plants or organisms and the susceptibility of the metal leaching [7]. In a single extraction, the following solutions are used: neutral solutions (H_2O, CH_3COONH_4), complex metal solutions (EDTA, NTA. DTPA) or high ionic strength solutions ($CaCl_2$, $MgCl_2$) which cause the release of adsorbed ingredients [8, 9]. Extraction with $MgCl_2$ solution can be a measure of the metals availability, which are deposited in sediments in natural environmental conditions [7]. Forms of metals released during the EDTA extraction are forms that are potentially available during the variable environmental conditions (pH, redox potential) [8]. In addition to the single extraction, a sequential extraction is used. This method is applied to separate forms of heavy metals, which can be released into the solution under various environmental conditions.

The first examples of sequential extraction of bottom sediments and soil are from the 1970s. Sequential extraction methods are based on the gradual release of metals in various forms. These methods involve a use of series of solutions with increasing leaching power. The most widespread and commonly used procedure for sequential extraction of five fractional metal fractions from bottom sediments is the Tessier procedure, currently used with minor modifications [10]. In order to obtain comparable results, which would allow for precise interpretation and application in environmental monitoring, it was essential to standardize the procedure for testing metal forms in bottom sediments. Recent years have brought attempts to standardize the research methods, eg. by the Community Bureau of Reference (BRC) [9]. In order to compare results, the European Commission, under the Standard Measurement and Testing Program (SM&T), has adopted common procedures for the heavy metals extraction, both for single and sequential methods. For the heavy metals single extraction it is recommended to use EDTA/CH_3COONH_4 solutions. This method allows to determine the metals bioavailability in sediments. Ure et al. [9] have developed a triple-step sequential extraction procedure called BRC in order to standardize the sequential speciation conditions. In the procedure approved by SM&T, Tessier’s two fractions were considered to be mobile equivalent. The proposed BRC method is expanded by introducing a fourth extraction step, that allows to determine the residual fraction.

Detailed environmental studies allow to control the natural processes that govern the heavy metals recycling cycle in surface water, including toxicity reduction and tracking the dynamics in the changes of the heavy metals forms in the water- sediment system. Forms of heavy metals (Zn, Cu, Pb and Cd) were investigated in bottom sediments, by using speciation analysis (single and sequential). This allowed us to assess the risk of bioavailable metals in surface water. In order to achieve the goal of the research, the sediments contaminated with metals were obtained from Utrata river (Poland) [11]. The obtained results allowed us to characterize the relationship between heavy metal forms present in bottom sediments and their environmental bioavailability.

Materials and methods. Bottom sediments

The samples of bottom sediments obtained from the Utrata river (Poland) were highly contaminated with metals. Zn, Cu, Pb and Cd contents were analysed in the surface layer of bottom sediments of 5cm thickness. Metal content was defined for dry sediments fractions with the particle diameter <0.090 mm. 1 g of sediment sample was taken from the separated fraction.

Determination of the heavy metals content in sediments

The content of the selected heavy metals (Zn, Cd, Pb and Cu) in the sediment samples was measured by flame atomic absorption spectroscopy (FAAS) based on the standard curves determined for a series of pre-prepared standard solutions by MERC company. Prior to the measurement, the dry mineralization and extraction of the sediment sample was performed. The detection limits for individual metals were calculated for the double standard deviation of five replicates in sediments (expressed as mg/ kg dry matter): Cd (0,005), Cu (0,03), Pb (0,05), Zn (0,01). In order to verify the correctness of the analysis and the measurement accuracy, a certified reference material Till-3 CRM with a known metal content was mineralized (Tab. 1). Metals recovery percentage from reference sediments varied between 93- 110%. The error resulting from the comparison of the analysis results, did not exceed 10%.

Table. 1.

Content of metals in the certified material Till-3

Metal	Mineralization in HNO3 + HClO4 (mg/kg)	Content in CRM (mg/kg)	Recovery %
Cu	21,5	23,0	93,5
Zn	45,5	43	105,6
Pb	21,8	20,3	107,4
Cd	5,9	5,3	111,3

Total metal content

The total metal content was determined in solutions obtained after mineralization of 1 g of air dried sediment with a mixture of acids (9ml HNO_3, 3ml $HClO_4$). The process of mineralization was carried out in a mineralization block, where the sample of bottom sediment and acids mixture were placed in a teflon pot. The solution obtained after mineralization was filtrated into a flask with volume of 100 ml.

Simple extraction

The effects of metal extraction from air dried bottom sediments using distilled water and solutions of: 1M $MgCl_2$ and 0.05M EDTA were determined in laboratory conditions. The extraction solution was obtained after mixing the sediment with an extractant in a weight ratio of 10g sediment/100 ml. The extraction was carried out for 1 hour. All metal assays were performed three times, giving as a result the average value.

Sequential extraction

Tessier sequence was used to determine the metal forms in the air dried bottom sediments [10]. In the extraction five fractions of metal bonds were isolated. Exchangeable fraction (F1) – 1g of a material was supplied with 8 ml of 1 mol/l $MgCl_2$ (pH 7) and mixed for 1h at room temperature.

The sample was then centrifuged and the metal concentration in the solution was determined. Fraction bound to carbonates (F2) – the residue from the first fraction analysis was treated with 8 ml of 1 mol/l sodium acetate acidified with acetic acid to pH 5 and extracted for 8h. Fraction bound to iron and manganese oxides (F3) – 20 ml of 0.04 mol/l $NH_2OH \times HCl$ in 25% acetic acid was added to the residue from the analysis of the second fraction and extracted for 8h at a temperature of 96˚C.

Fraction bound to organic matter (F4) – the residue from the analysis of the third fraction was mixed with a mixture containing 3 ml of 0.02 mol/l HNO_3 and 5 ml of 30% H_2O_2 acidified to pH 2 and heated for 2 h at 85˚C. Then the solution was cooled and supplied with 3 ml of 30% H_2O_2 acidified to pH 2 and heated at 95˚C for3 h. After cooling 5 ml 3.2 mol/l of CH_3COONH_4 solution in 20% HNO_3 was added and the sample was mixed for 0,5h.

Residual fraction (F5) – the sample after the last extraction was mineralized in a mixture of acids (5 ml HNO_3, 2 ml $HClO_4$ and 1 ml HF).

Results and discussion

The research results showed that the sediments contained heavy load of heavy metals. The average total metal content in sediment samples was equal to 246,6 mgZn/kg, 10,1 mgCd/kg, 148,4 mgPb/kg, 132,2 mgCu/kg dry matter.

Results of single extraction, using three extractants (H_2O, $MgCl_2$ i EDTA) are presented in Figure 1. The water-leaching process showed a considerable degree of their mobility. 4% Cu, 7% Cd, 10,5% Pb and 20% Zn passed into water. Extraction efficiency with $MgCl_2$ solution allows to put metals in the following order: 2,3% Cu, 3% Zn, 13%Pb and 41% Cd. Metal extraction with 0.05M EDTA solution removed from sediments on average 11% Cd, 27% Pb, 34% Zn and 60% Cu. The most effective extractant for copper and zinc was 0.05M EDTA solution, however, it was not efficient in extraction of lead and cadmium. The most effective solution for releasing Cd from sediments was magnesium chloride, neutral and of high ionic strength. Pb was released from the sediments to a similar extent by magnesium chloride and water as extractants. Like Zn and Cu, Pb was extracted most efficiently by the EDTA solution.

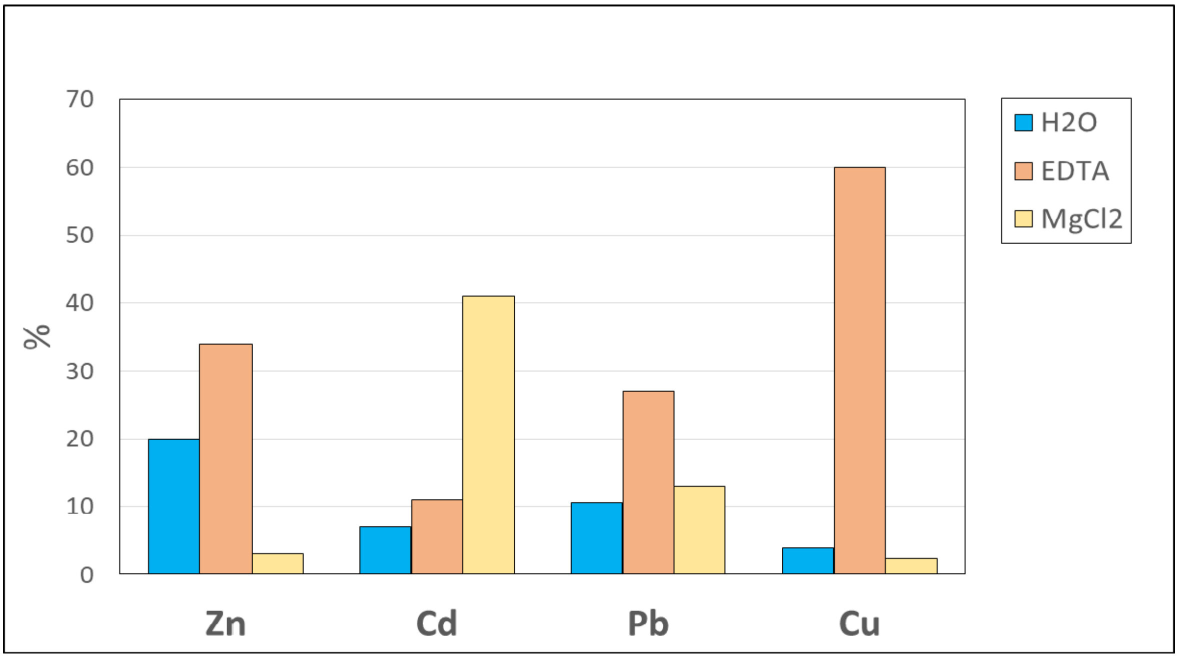

Fig. 1. The percentage of metals extracted from the sediments by water, EDTA and $MgCl_2$.

All bottom sediment samples were subjected to Tessier specimen analysis measuring the Zn, Cu, Pb and Cd content. Measurable metals bound in 5 fractions (ion exchange, carbonate, adsorption, organic and residual fraction) showed different bioavailability in aqueous environment [12].

Zinc was mostly bound in the hydrated fractions of Fe/Mn oxides (15,7–49,7%). The comparable amount of this metal was observed also in the residual fraction (8,3-48,8%, average-30%). A significant amount was also in the carbonate fraction (7,7–46,3%). This zinc driving separation between sediment fractions may indicate the mobility of contamination containing this metal (fig. 2). Copper was bound strongly in the organic fraction (average 43%) and the rest fraction (average 42%) (fig. 2). Similar levels of copper binding in sediments were observed by Akcay et al. [2]. They obtained a high copper content in the residual fraction (F5) in sediment samples from Buyak Menderes and Gediz rivers. In the Utrata river sediments, copper showed low content in mobile fractions (exchange, carbonate and adsorption), where the total amount for these three fractions was maximum 23%. Similar results have been obtained for mobile fractions by other researchers: the copper proportions in the first three fractions (F1+F2+F3), with high mobility, did not exceed 15% of the total content [13].

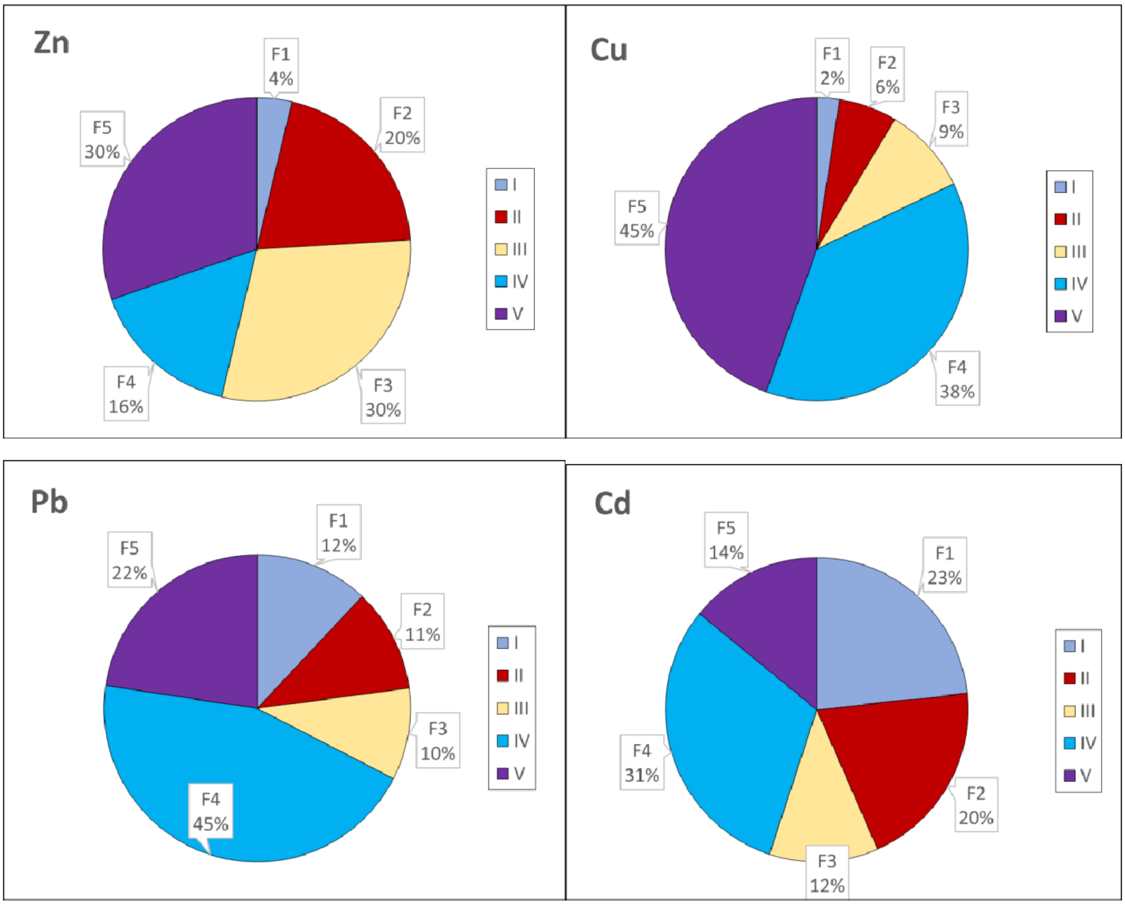

Fig. 2. Percentage of zinc, copper, cadmium, lead forms in the bottom sediments of Utrata river.

The highest amount of cadmium was observed in the organic fraction and in the mobile fractions: exchangeable and carbonate fractions (fig. 2), which proves the strongest bond of cadmium to these fractions. In the other two fractions, the percentage was: in adsorption 3-23% and in the residual fraction 6- 25%. The cadmium percentage in mobile fractions (F1, F2, F3) exceeded 50% and even reached over 60% of the total content. The high content of reactive cadmium fractions was also obtained by other authors [14]. The lowest involvement in the residual fraction (F5) for Cd was 14%. Lead, like copper was poorly bound in the exchangeable fraction, stronger in carbonate and adsorption and the strongest bond was observed in organic fraction (fig. 3). In most conducted studies, the results show a high lead affinity for adsorption fraction [15, 16]. The obtained results for Utrata river bottom sediments indicate a different lead binding ability. Lead present in the sediments remained in high percentages in low reactive fractions. Very low involvement in the residual fraction (fig. 2) was stated for lead (average 23%). However, the three bioavailable fractions (F1, F2, F3) periodically contained more than 50% Pb.

Heavy metals in sediments are separated between geochemical forms and the bonding degree strongly depends on the sediment composition [18]. Metals from anthropogenic sources are considered to be labile associated with the solid phase surface [19], leading to their mobility and bioavailability. Studies have shown a high cadmium content in mobile bottom sediment fractions from Utrata River comparing to other metals. Cadmium, which is strongly bound in these sediment fractions (more than half of the total amount), can be released into water, resulting in an increase of bio- absorbable forms which are toxic to biomass. As a result, the whole environment and the whole food chain is affected. The amount of exchangeable form of Zn and Cu in sediments was ineligible. The conducted speciation analysis showed the absolute dominance of the organic fraction in copper and lead binding. Cadmium as well showed strong affinity for this fraction.

The metal binding in individual fractions can be ordered in the following order:

F1: Cd > Pb > Zn > Cu
F2: Zn > Cd > Pb > Cu
F3: Zn > Cd > Pb > Cu
F4: Cu > Pb > Cd > Zn
F5: Cu > Pb > Zn > Cd

In the Mexican Lerma- Chapala Watershed study, in which only total concentration was analyzed, they found that the sediments transported by the Lerma river to Chapala lake are the final deposition destination of Cd, Cr, Ni, Cu, Pb, Zn. A proper risk assessment of the metal migration from contaminated sediments to water in Chapala lake was performed only in the following studies, using a five-step sequence of sequential metal extraction [20].

The metal separation results in Utrata river sediments showed that the exchangeable fraction represented between 11% and 26% of the total cadmium content. The second metal with a significant participation in this fraction was lead (6 - 12%). For zinc and copper the content in this fraction was much lower, respectively 1,5- 5% and 1,4-3%. Such participation in the F1 fraction indicates that cadmium and lead pose a high risk for flora and fauna located at the bottom part of the river. Percentages of cadmium (13% -24%) and lead (4-22%), similar to those exchangeable fraction, were found also in the carbonate fraction. Zinc also showed a high participation of carbonate binding (8 - 46%). This proved that carbonates fraction had a strong affinity for the testing metals [21]. For copper, the percentage in F2 was very low (1,9% -5,6%). A high amount of carbonates (average 12%) was found in contaminated sediments of Utrata river, as well as a significant content (up to 22%) of lead in this fraction. Cadmium binding in the reactive carbonate fraction occurred also in the sediments of Volvi and Koronia lakes ([17] and in the river within Iverian Pyrite area on Iberian Peninsula [22]. The carbonate fraction contained a significant amount of total cadmium and lead content in Poraj reservoir sediment [23] and Povang lake [24], lead in Rybnicki reservoir [25] and in reservoir sediments of Kozłowa Góra [26] and cadmium in sediments analyzed by Yang et al. [27]. Our own studies have confirmed the studies of Billon et al. [28], proving that metal ions can be absorbed on the carbonated mineral's surface and then incorporated into crystalline structure, eg $Cd_xCa_{1-x}CO_3$. The Cd contribution in the carbonate fraction may be due to the similarity of cadmium and calcium ions. These metals have similar ionic ion radius Cd (0,97A) and Ca (0,99A), so co-precipitatation of cadmium and its incorporation into the crystalline calcite network can occur in the environment [29]. Turka's studies [30] proved that carbonate fraction is dominant for Pb speciation only when carbonates are a minor part of the sediment composition. Singh et al. [31] observed a similar carbonates role in binding Pb and Zn in contaminated sediments of Gomti river, a tributary of the Ganges.

Results, obtained in my own studies, showed the strongest binding of zinc (16 – 50%) in the fraction of hydrate oxides of Fe/Mn, which is sensitive to redox potential changes. For the residual metals, the average participation in the adsorption fraction was 14% Cd, 8,5% Pb and 7,5% Cu. Because of large surface, hydrate oxides Fe/Mn are one of the most important geochemical phases affecting the mobility and metal behavior in sediments [32]. This was confirmed under the waste water environment conditions of Utrata river, where the precipitation of sparingly soluble iron forms (hydroxides, phosphates) was observed. Zinc sorption may occur on the precipitates [33]. Many studies have confirmed the high adsorption efficiency of hydrated Fe/Mn oxides in zinc removal process from water [33, 34].

In studies of bottom sediments from Utrata river, similar to Besser et al. [35] studies, a high content of Cu (43%), Pb (43%) and Cd (37%) in organic and sulfide fractions and low of Zn (14%) was confirmed. Wang et al. [34] confirmed the copper presence mainly in organic sulfide fraction. The organic fraction of metals is often assessed as stable, with low hazard. Basing on that, it can be assumed that the concentration of metals in interstitial and benthic water and the concentration of dissolved forms decreases, and thus the toxicity of these metals decreases. Current opinions differ on the metal toxicity bounded by organic substances. Yao et al. [36] studies have shown that metal complexation by organic matter, which serves as nourishment, can increase its toxicity for annelids (oligochaetes). On the other hand, in sediments of shallow Utrata river, where superfluous water layers are well oxygenated and varying hydrological conditions are observed, a high amunt of Cd in organic and sulphide fraction (F4) may indicate toxicity of Cd for benthos invertebrates. It is caused by the process where CdS will be oxidized to the soluble form of $CdSO_4$ in aerobic conditions [34].

The content of the analysed metals in the residual fraction, constituting the insoluble fractions, varied in Utrata river sediments. Metals were associated with this fraction with different strengths for zinc, copper, lead and cadmium, respectively about 26%, 42%, 37% i 13% of total content. This part of metal is theoretically inaccessible to microorganisms and should not be activated in predictable time. In sediment studies from Poraj reservoir, which is tributary with Warta river waters [23], Kozłowa Góra reservoir sediments [26], sediments from Dongting lake [36] or Taihu lake [37] have shown a significant role of residual fraction in binding zinc process. Fityanos et al. [17] used a five- step metal extraction procedure to evaluate the assessment of sediment contamination by six metals (Cd, Cr, Pb, Mn, Zn, Cu) in two lakes (Volvi and Koronia), in northern Greece. Their results showed that Cd, Cr, Cu and Pb were mainly associated with the residual fraction and, to a lower extent, with carbonate fraction, posing a low risk of secondary lakes contamination.

A single extraction was performed to confirm the results of sequential extraction of the labile metal binding in sediments. The degree of water-leaching of lead and zinc was more than 10 percent, while cadmium and copper up to 10 percent. This has confirmed the labile nature of the metal binding in sediments and high probability of passing them to the dissolved phase. Using a $MgCl_2$ solution with stable pH and high ionic strength for extraction, a higher degree of elution with respect to cadmium (>40%) and lead (>10%) was obtained for the extraction and low for copper and zinc (<5%). Extraction with $MgCl_2$ showed higher results than extraction with water, which was due to the character of magnesium chloride and the competitiveness of heavy metal cations with respect to the large Mg^{2+} ion. High concentrations of metals were obtained in EDTA extracts. The affinity for the chelating solution was predominantly copper, passing to the solution in about 60%. Lower extraction efficiency was found for zinc and lead, the lowest for cadmium.

Significant metal leaching ability with water and used solutions, indicates the presence of metals in mobile forms, which is typical for short time deposited sediments. Mobility of the metals bound in sediments depends on their individual properties and the composition of the over sedimentary water and the variable character of sediments. Under the conditions simulating minor environmental changes (magnesium chloride effluent), more toxic metals (Cd and Pb) were released, indicating a high bioavailability of their forms. Similar metal behaviour was observed in studies and research conducted in the Amur, Rhine and Dommel river valleys [38, 39, 40] and in the middle part of Vistula valley [41]. Metals reaching the aquatic environment are deposited in bottom sediments and temporarily immobilized, but may pose a threat to aquatic life. Under favourable conditions, metals may be released back into the water and then incorporated into the trophic chain and participate in further biological cycle stages. Changing environmental conditions can transform metal forms into sediments and change their bioavailability. Therefore, knowledge of the metal form contribution in sediments is necessary to describe their mobility and bioavailability in the aquatic environment as well as, in risk assessment. The metal tendencies for migration depend on their sediment forms, which are indicators of long term changes of water pollution and biological and chemical changes in the aquatic environment.

Conclusions

Heavy metals accumulation in the surface sediment layer is an ecological reflection of the rivers conditions and as well as the intensified anthropopression associated with the progressive urbanization of the catchment area. Metal fractionation showed different strength in metal binding processes in five bottom sediment fractions. Significant amounts of metals were bound in mobile fractions, indicating their high bioavailability. Possibility of heavy metal remobilisation from the bottom sediments to deep water, indicates a postponed environmental hazard. An important element of the bottom sediment research testing tool is use of more than one analytical method (simple and sequential extraction). Conducted research proved that sequential analysis of metal specimens should be co-used with single extraction to evaluate the metals transformation in biogeochemical cycles in aqueous environmental, which significantly reduced ambiguous results and misinterpreted them. The results of single and sequential extraction in conducted research, proved correct, indicating the potential possibility of metal migration in water-sediment system as a result of water quality parameters, indicating their mobility and bioavailability.

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Modification of catalyst of the direct chlorination of ethylene into 1,2-dychloroethane

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***Abstract* – new improved catalytic system for the process of the direct chlorination of the ethylene is proposed and investigated. New catalytic system increases productivity of the reactive volume and allows to decrease negative influence of production on the environment.**

Keywords: catalytic system

Introduction

As it is known, as catalyst for the reaction of direct chlorination of ethylene into 1,2-dychlorethane (DCE) is used chloride of iron (III), that is promoted by sodium chloride in concentrations of 1000 ppm and 20 ppm respectively, meaning at ratio 1:20. Under such conditions amount of created DCE is 98,2-99,4%, and as by-products are created vinyl chloride, four chloro carbon, 3-chloro ethane, 3-chloro ethylene and others.

During preparation of catalytic system [$FeCl_3$-NaCl] certain attention should be paid to the size of sodium chloride particles (d≤60 mcm), because its solubility in DCE is low even under such dispersion of sodium chloride and time needed for creation of solution is 2 hours. It is also worth mentioning that catalytic complex breakes into components under temperatures lower than 50 °C leading to decrease in activity of catalytic system.

Results and discussion

We have prepared mixtures of sodium chloride with addition of 10% sodium salt of perfluorosulfonic acid, as a stabilizer of complex (modifier) of the following fraction composition:

Table 1

Fraction composition of the prepared mixtures.

Date	Moisture, %	Fraction composition,%			
		0,2 mm	0,09 mm	0,045 mm	Less than 0,045 mm
27.07.2018	0,15	46,1	46,9	6,5	0,3
12.11.2018	0,16	59,3	24,5	14,9	0,4
12.03.2019	0,12	1,0	2,2	89,3	7,5

After dissolution of iron chloride in reactor was added needed amount of sodium chloride with modifier and after 2 hour mixing catalytic solution was transferred to the reactor of direct chlorination of ethylene.

According to the data of the long-term experiments concentration of sodium ions in the reactor of direct chlorination was increasing during all period of experiment from 8 ppm to 33 ppm, and after stoppage of activator addition it decreased to 10-15 ppm.

Analysis of the ratio of ions [sodium:iron] showed that it also increased during experiments and reached previously set indexes.

Symbiotic behavior of change of concentrations of ions of iron and sodium during constant increase of their ratio proves positive influence of modifier on catalytic complex.

Analysis of pureness of DCE in reactor of direct chlorination shows its increase from 98,9% (2 January) to 99,3%.

Conclusion

Thus modification of the catalyst of direct chlorination of ethylene allows to increase selectivity of creation of 1,2 – dychloro ethane and decrease amounts of by-product 3-chloro ethane, that decreases amount of chloro organic compounds on the burning stage and leads to increase of ecological safety of the production.

Decreasing of the level of ecological pollution at processing of chloral-organic wastes of the production of 1,2-dychloro ethane

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Abstract – one of the main challenges for the Ukrainian industry is adopting of the modern environmental standards of production. One of the most promising ways of reaching of those aims is improvement of existing technological schemes by use of new catalytic systems.

Keywords: catalytic system, environmental standards

At the production of 1,2-dychloro ethane by direct chlorination of ethylene amount of obtained DCE is 98,2-99,4%, and as by-products are created created vinyl chloride, four chloro carbon, 3-chloro ethane, 3-chloro ethylene and others, that after rectification are transferred to the burning stage. During this stage are created products such as chloral hydrogen, that requires additional purification of the burned gases from harmful additives.

During use of sodium salt of perfluorosulfonic acid, as modifier for catalytic system, ammount of 3-chloral ethane decreases from 0.46% to 0.30% or in 1.53 times, and this dependence is directly proportional to the increase of sodium amount in catalytic solution (Fig.1).

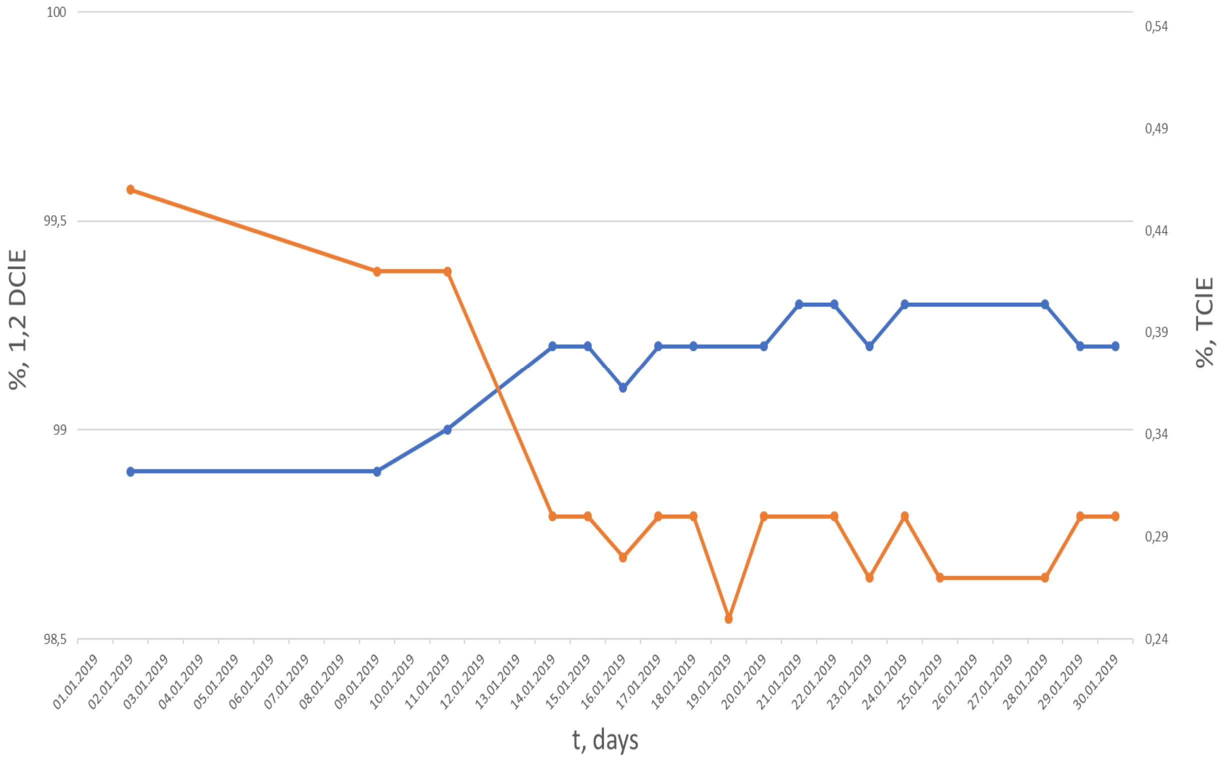

Fig. 1. The dependence of the yield 1,2 dichloro ethane (blue line) and trichloroethane (orange line) on time.

This way adding of catalytic complex modifier decreases amount of created by-products and therefore negative influence on environment.

CONTENT

SPONSORS AND PARTNERS

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KARPATNAFTOCHIM Ltd. was founded in October 2004. Legal address ID code: 33129683.

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StarMax

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Private enterprise «StarMax» is located in the city of Chernivtsi (Ukraine) in an ecologically clean area in the foothills of the Carpathians and is engaged in the cultivation and sale of mushrooms of champignons. The enterprise has been officially put into operation, the operational permit has been obtained at the State Sanitary and Epidemiological Service of Ukraine, hygienic conclusions have been made on the enterprise products and certificates of conformity. All products are manufactured according to state standards, norms and rules.

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TO THE MEMORY OF THE OUTSTANDING SCIENTIST AND PEDAGOGUE OF LVIV POLYTECHNIC GREGORIY ABRAMOVYCH AKSELRUD

To the memory of the outstanding Scientist and Pedagogue of Lviv Polytechnic

Jaroslaw Gumnitsky

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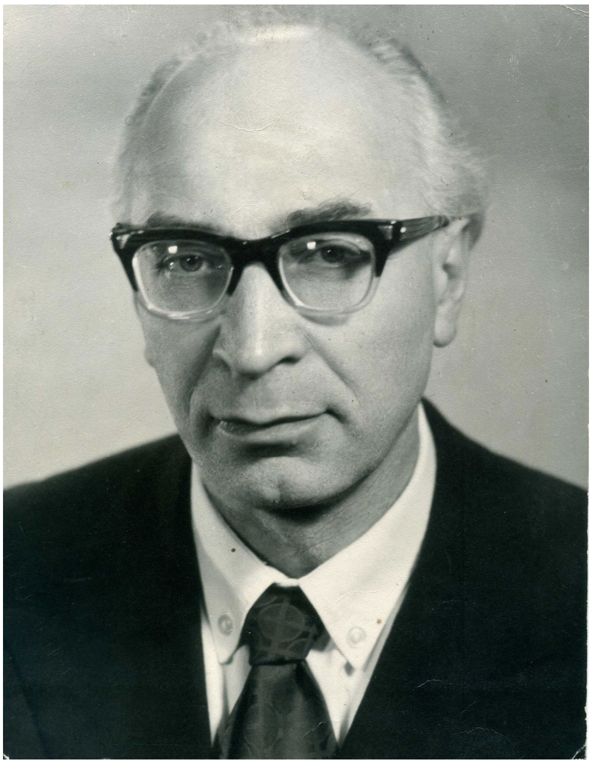
The article is devoted to the 100th anniversary of the birth of the Doctor of Technical Sciences, Professor, Honored Worker of Science and Technology of Ukraine, Head of the Department of Processes and Apparatuses of Chemical Production (now – the Department of Chemical Engineering) Gregoriy Abramovych Akselrud.



2019 year is for the Department of Chemical Engineering significant, because it marks a number of anniversaries. The first jubilee to be called the anniversary of the department itself, which was founded in 1949 and this year celebrates its 70th anniversary. The best honor of this anniversary will be the international scientific conference to be held in June 2019. Together with this, the scientific glory of the department was brought by doctors of technical sciences, professors, whose anniversaries came from this year.

On May 1, 2019, we celebrated the 100th anniversary of the birth of the Doctor of Technical Sciences, Professor, Honored Worker of Science and Technology of Ukraine, Head of the Department of Processes and Apparatuses of Chemical Production (1967 - 1987) Gregoriy Abramovych Akselrud. He graduated of the Kiev Polytechnic Institute and the Moscow Institute of Chemical Machine-Building (1944), he binds his fate with Lviv Polytechnic since 1949. Once again I emphasize that this was the time when the Department of Processes and Apparatus was founded and he was the only certified specialist in this specialty at the newly formed department. He worked at this department from assistant to the doctor of sciences, professor, head of the department. In 1955 he defended his Ph.D. thesis, and in 1967 – a doctorate.

His scientific research professor Akselrud G.A. devoted to processes of mass transfer in systems with solid phase. We noted that the science of processes is multifaceted, including hydrodynamic, thermal, mass exchange and mechanical processes, and each of the listed processes is split into specific concrete processes used in the chemical, food, hydrometallurgical, pharmaceutical industries, and more recently in environmental technology. His research includes dissolution processes, solid phase extraction, adsorption, and diffusion-controlled chemical reactions of solid phase with a liquid reagent. The listed processes are extremely widely used in the industry. It is enough to produce fertilizers, products of organic synthesis, wastewater treatment, aluminum production, etc.

Science is divided into applied and theoretical. Professor Akselrud was a prominent theorist. This required knowledge not only of the physical foundations of the processes under study, but also the knowledge of mathematics. Being a Ph.D., he enrolled in a mathematical seminar at the Faculty of Mathematics of the I. Franko University, because the knowledge of higher mathematics, obtained him during the war years, was not enough.

Professor Akselrud G.A. developed a theoretical analysis of the components extraction from isotropic and anisotropic particles in the diffusion point of view, especially during extraction of useful components from plant cells. If we take into account that the bulk of medicinal raw materials is based on extraction from plant material, then it becomes clear the importance of its theoretical research. Very often, his decisions were based on an operating method based on Laplace transforms. Every work carried out under his leadership included an obligatory element of the method of intensifying this process. These were mechanical and pneumatic mixing, low-frequency pulsations of the medium, vibration treatment, ultrasound, electric and magnetic field, boiling layer, attractors, rotary-turbulent apparatus and others. These studies were important for chemical technology, but interesting for other technologies. He published more than 500 scientific articles, as well as methodological developments and lecture notes. Under his leadership, more than 60 candidate's theses and 10 doctoral theses have been defended. There are some of them: Yavorsky V.T., Semenyshyn Y.M., Gumnytsky Y.M., Molchanov AD, Kalinovskaya O.P., Maziak Z.Yu., Dubinin AI, Khanyk Ya.M.

They published 8 monographs, a series of which were translated into Polish, Hungarian, English, Bulgarian. The last monograph "Mass exchange in the system of solid-liquid-liquid" was written by Akselrud G.A. and Gumnytsky Ya.M. from the Ukrainian side and by Petrus R. and Piantakovskij V. from the Polish side has published in Polish in 1998. It should be noted that the chemical engineering in Poland is developed at a high level, and because our monograph in Poland took the second place among the scientific publications and was awarded with a diploma and a second monetary prize, it testifies to the high scientific level of the monograph and the merit of Professor Akselrud who directed it an international team of authors.

For 20 years the professor headed the department, created a team of scientists. At this time, the department employed 7 doctors of sciences, professors. A Doctor's Council was established to defend candidate and doctoral dissertations. The department was headed by a board of extraction processes from the solid phase at the Academy of Sciences.

The scientist successfully combined the scientific work with the training. His lectures were always distinguished by a high scientific level, novelty, problematic, psychological and methodological presentation, the use of technical means at these times. He was deeply erudite man, knew literature, liked classical music, knew history and the Bible.

Ukraine appreciated the contribution of Professor Akselrud G.A. in the development of science and training specialists for the national economy, having awarded him the title of Honored Worker of Science and Technology of Ukraine.

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