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Federal Research Center “Crystallography and Photonics”
of the Russian Academy of Sciences
M.V. Lomonosov Moscow State University
ZAO “Schag”
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"Supercritical Fluids: Theory and Practice"

The 10th Scientific and Engineering Conference
with International Participation
"Supercritical Fluids: Fundamentals, Technologies, Innovations"

BOOK of ABSTRACTS

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G.A. Krestov Institute of Solution Chemistry, ISC RAS

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SCIENTIFIC PROGRAM

The scientific program of the X Scientific-practical conference with international participation "Supercritical Fluids (SCF): Fundamentals, Technologies, Innovations" include:

8 plenary lectures (40 min), 8 key lectures (30 min), 38 oral reports (20 min), 25 oral reports by young scientists (10 minutes), 50 poster presentations and 20 correspondence reports, addresses a wide range of fundamental and applied issues related to development and application of supercritical technology in the directions:

- Physical and physicochemical bases of processes in SCF media
- Analytical applications, analysis and diagnostics of SCF media
- Chemical processes in SCF media
- Synthesis, separation and cleaning of materials (including natural materials)
- Creation of functional and composite materials:
  - Materials for micro-, nano- and optoelectronics
  - Multi-purpose polymer materials
  - Materials for biomedicine and pharmacy
  - Construction materials
  - Nanocomposite, nanoporous and ultra-disperse materials, aerogels
  - High energy materials
  - High purity materials
  - Catalysts
- Processes in water at sub- and supercritical state
- Social aspects of introducing SCF technologies, ecology
- Educational programs and specialist training

The conference events will include the Xth All-Russian Workshop of Young Scientists “Supercritical Fluid Technologies in Solving Environmental Problems” and a round table on educational programs in the sphere of SCFT.

The conference languages are Russian and English.
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The date of this conference is almost exactly the 35th anniversary of my meeting Victor Nikolaievich at a conference not far from Prague. Rapidly we became firm friends and collaborated in the field of supercritical fluids for almost 30 years. This short and highly personal lecture, which sadly has to be delivered by video, will outline some of our joint work, particularly in detection of phase transitions [1]. I will also highlight what, from my perspective as a foreign scientist, were some of Victor’s main contributions to supercritical science in Russia. There is no doubt that his contributions have been immense. I very much hope that together we can build on the wonderful foundations that he laid to inspire new generations of scientists and to take supercritical science in Russia to ever greater success.

Acknowledgements: I thank all of my colleagues, collaborators, co-workers as well as our technicians. In particular, I thank Professors Mike Georg and Steve Howdle for their support. I also thank the Engineering and Physical Sciences Research Council, The Bill and Melinda Gates Foundation and The Garfield Weston Trust for financial support.

MOLECULAR MAGNETS FOR MATERIALS OF NEW GENERATION
INFORMATION SYSTEMS

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The possibilities of application of the bistable organic and metal complex molecular systems with a magnetic response to external stimuli for use as molecular switches and high-capacity non-volatile molecular memory (MRAM) are considered. The main mechanisms of switching of spin states are presented. The prospects of obtaining monomolecular magnets and the use of transition metal complexes with redox ligands as quantum qubits are considered.
We have exploited the low viscosity and high diffusivity of scCO$_2$ to allow new approaches to nanostructured polymeric materials prepared directly in scCO$_2$ using dispersion polymerisation techniques. A key focus has been the use of controlled polymerisation to deliver template materials and to exert fine control on the polymeric morphologies obtained from lamellar through to nanoporous materials.

A further target has been the development of new approaches to functional and renewable polymers and to do this we have developed a wide range of new monomers based on natural materials (terpenes) and also developed a new range of surfactants grown from natural starting materials, again using controlled and even enzymatic approaches in scCO$_2$


4. G. B. He, Thomas; Alauhdin, Mohammad; Fay, Michael; Liu, Xin; Schwab, Simon; Sun, Chenggong; Howdle, Steven M., *Polymer Chemistry*, 2018 **9**, 3808-3819.


DECIPHERING THE LANGUAGE OF PHOSPHOLIPID-BASED COMMUNICATIONS: ROLE IN CELL DEATH/ELIMINATION AND REPROGRAMMING

Valerian E. Kagan

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Fidelity and quality control of biological systems depend, to a large extent, on the reprogramming or elimination of unnecessary or harmful cells and their components. Reprogramming is commonly engaged when the responses to changing environments are still reversible while elimination is triggered usually when the damaging or toxic materials exceed the repair capacities of cells. For a long time, cell death has been viewed as a catastrophic and mostly chaotic chain of events. Over the last 3-4 decades, this point of view has changed as experimental biology has discovered several organized and highly regulated cascades of cell death, thus “erasing” the differences between reprogramming and death. Insufficient levels of elimination of harmful materials lead to the accumulation of antigenic/genotoxic materials - typical of cancer or auto-immune diseases; vice versa, exceedingly massive elimination leads to tissue and organ injury - eg, brain injury, sepsis, radiation injury, chronic degenerative diseases, etc. In addition to the general biological, philosophical and even social aspects of the interpretation of death, this dualism of the elimination processes is remarkably important in biomedicine and will be discussed in the current lecture. In particular, not only the philosophy but also the effectiveness in controlling the fine balance between preservation and elimination of the death signals hence controlling the transition of the biological units from live thermodynamically open systems into dead material is at the basis of our understanding of the etiology and pathogenesis of disease. I will focus on molecular mechanisms of several death programs with the particular emphasis on the regulation and the signaling role of lipids and their oxidation products as a part of high effective and rich language used by individual cells and their communities to eliminate and/or reprogram unnecessary or harmful cells.
In the last quarter of a century, there is a gradual transition from traditional “inert” biomaterials that perform primarily mechanical functions to new, so-called, functional biomaterials. Functional biomaterials are used in the development of medical devices, in tissue engineering, in drug delivery systems, as well as in bioimaging. Understanding the fundamental mechanisms of cell-biomaterial interaction has allowed to formulate the major requirements for the functional biocompatible materials. First of all, the materials should have the appropriate functional groups that control the processes of cell proliferation, migration and differentiation. In addition, the materials should have optimal viscoelastic characteristics as well as optimal mass transfer characteristics of both oxygen and various biological compounds. In many cases, functional materials can be carriers of physiologically active compounds, systems for gene therapy and systems for bioimaging. Molecular design and fabrication of such materials both at the nanoscale and microscale is the most important problem in the development functional biomaterials. Supercritical fluids appear as an important alternative to the conventional methods for processing functional biomaterials.
In this lecture, devoted to the memory of Prof. Victor Bagratashvili, I will explain what we were doing together in the field of laser printing.

We started from two-photon polymerization (2PP) technique, which allows direct writing of 3D microstructures (scaffolds) into the volume of photosensitive biomaterials, which is very important for different biomedical applications. Thanks to Victor and his efforts, at present this technology is actively used in Russia in different R&D projects.

Laser generation and printing of nanoparticles was another interesting research field, where we planned novel joint projects and started working together. I will demonstrate laser printing and arrangement of spherical metal and dielectric nanoparticles in a very precise manner. These nanoparticles and nanoparticle structures are characterized by unique optical properties. For example, laser printed Si nanoparticles with sizes in the range of 100-200 nm in diameter exhibit pronounced electric and magnetic dipole resonances within the visible spectral range.
Optical applications of these nanoparticles for realization of metasurfaces, second harmonic generation, etc. will be discussed.

Laser printing of living cells and microorganisms was our favorite project, where we started working together with Victor. I will report on our progress in this rapidly developing field.
The contribution presents recent advances in the processing of biopolymer aerogels with a focus on their large-scale production. We begin with a short introduction into fundamentals of the gelation, solvent exchange and supercritical drying. An overview of physical properties and corresponding application areas will be presented. We proceed with existing and emerging concepts towards large-scale production of biopolymer aerogels. In the concluding part we discuss open scientific and engineering questions related to the topic.
Injection of supercritical CO$_2$ into deep geological formations and depleted oil and gas reservoirs is an effective method for enhanced oil recovery and a promising pathway for reducing anthropogenic CO$_2$ emissions contributing to the global climate change. One of the anticipated problems for the large-scale application of geological carbon capture and sequestration (CCS) technologies is the potential degradation of cement wellbore casings due to their exposure to supercritical CO$_2$, which can pose significant environmental risks. To minimize these risks and to optimize stable and reliable CCS operations, a detailed molecular level understanding of the interactions between cement and CO$_2$ rich fluids is necessary, as well as clear understanding of the fluid transport pathways in wellbore cement materials. In addition, the long-term effectiveness of fluid CO$_2$ confinement is strongly dependent on its interaction with host rocks (mostly sedimentary minerals, such as various clays, quartz, carbonates, etc.), rock nanoporosity, temperature, pressure and other factors.

Methods of atomistic computational modeling are very well suited for providing such internally consistent molecular scale information on the interaction of supercritical CO$_2$ with various materials, thus greatly improving our understanding of the specific effects of the substrate structure and composition on the structure, dynamics and
reactivity of the interfacial and nano-confined CO$_2$ rich solutions. In this talk, a brief overview of our most recent atomistic modeling results will be presented for several cement-related and clay-related systems, in contact with CO$_2$-H$_2$O and CO$_2$-CH$_4$ mixtures under $T/P$ conditions typical for geological CO$_2$ sequestration and application of supercritical CO$_2$ for enhanced oil recovery.

*) This project has received funding from the European Union’s Horizon 2020 research and innovation programme under grant agreement No 764810.
Highly porous polymer matrices are one of the prospective platforms for creation of novel functional materials for biomedical applications. One of the possible approaches to synthesis of these matrices is the foaming of plasticized polymer under the decrease in the pressure of a plasticizing subcritical/SCF agent. Carbon dioxide is often used as such agent, and the raw polymer materials for synthesis of bioresorbable matrices are typically the polylactide or polycaprolactone. The reason for use of these polymers, in addition to biocompatibility and bioresorbability, relates to the high efficiency of plasticization in the carbon dioxide atmosphere. Empirical data obtained by various research groups show that the major influence on the structural properties of synthesized porous matrices is caused by the initial pressure and the pressure decrease rate in the course of foaming. Despite a large amount of the existing experimental data on the supercritical fluidic synthesis of porous polymer matrices, there are no any adequate models describing influence of the foaming modes and polymer properties on the structural characteristics of synthesized matrices. In this work, we present the results of interpretation of the experimental data on the quasi-adiabatic and quasi-isothermal foaming of bioresorbable polymers using a model based on the Ross equation of state for the foam [1]. The following modification of the Ross equation is considered:

\[ P_{\text{ext}}V + K^* \Sigma = K^* U_{\text{int}}, \]  

where \( P_{\text{ext}} \) is the external pressure in a reactor, \( V \) is the volume occupied by a foamed polymer, \( \Sigma \) is the surface energy of interfaces between the bubbles, \( U_{\text{int}} \) is the internal
energy of gas inside the bubbles; \( k' \) и \( k'' \) are the normalization coefficients. Equation (1) is considered for the initial and final states of the expanding foam. The sounding feature is the stability of the right-hand side of Eq. 1 in the case of quasi-isothermal expansion and the strong dependence of the \( k''U_{int} \) increment on the initial and final values of pressure under quasi-adiabatic expansion. Figure 1 displays the dependencies of the normalized parameter \( P_{ext}V \) on the time lapse in the case of quasi-adiabatic expansion of the polylactide foam with various values of the initial pressure (the plasticizing/foaming agent is carbon dioxide).

Non-monotonic behavior of \( P_{ext}V \), which takes place in the case of values of the initial pressure in the vicinity of the critical pressure \( P_c \) for carbon dioxide, is caused by a positive increment of the specific internal energy of carbon dioxide in the course of polylactide foam transition from an initial to final state under these conditions. Analysis of the structure of synthesized matrices provided using the optical microscopy and low-coherence reflectometry has shown that the sufficiently larger structure fragmentation (and, correspondingly, smaller pores) occurs in this case in contrast with the foaming modes provided with the initial pressures strongly differing from \( P_c \).

The obtained experimental data on the quasi-adiabatic and quasi-isothermal foaming of bioresorbable polymers using subcritical/SCF carbon dioxide in combination with the results of data interpretation using the considered model allowed the choice of foaming modes providing the required structural parameters of the synthesized porous matrices.
This work is supported by the grant № 18-29-06024 from the Russian Foundation for Basic Research.

Synthetic polymers based on polylactides and polylactoglycolides, which degrade in the human body in the timeframe of a few weeks to several months, yielding nontoxic lactic and glycolic acids, have shown promise as materials for manufacturing temporary prosthetics for various tissues and organs (i.e., matrices). The polymer can be doped with biologically active substances: anti-inflammatory, antitumor, etc., which are released into the body as the matrix decomposes. Technologies based on supercritical carbon dioxide can be used in the production of doped polymers, allowing impregnation under mild conditions without employing toxic solvents. The kinetics of drug release is determined by the mechanism of hydrolytic degradation of the polymer, the architectonics of the sample, as well as the distribution of the dopant in the polymer matrix. Degradation of polyesters can lead to significant acidification of the inner regions of the matrix, which in some cases leads to decomposition of the drug substance.

The present work is devoted to the design of D,L-polylactide porous matrices and films and their concurrent impregnation with biologically active substances in supercritical CO\(_2\). Compounds with paramagnetic nitroxide fragments in their structures were used as dopants. This approach allows testing of the obtained materials and establishing the kinetic regularities of their hydrolytic degradation by means of electron paramagnetic resonance (EPR) spectroscopy. EPR makes it possible to observe swelling of a polymer in a supercritical solvent and its relaxation at pressure release, to assess the uniformity of the dopant distribution in the formed matrix at macroscopic and molecular levels, to establish the kinetic regularities of the release of a biologically active compound in aqueous medium, to characterize the
degree of acidification of the internal regions of the polymer material, and to study pore formation and degradation of the polymer nondestructively.

The report will present the diagnostic results for D,L-polylactide materials containing the stable nitroxyl radicals TEMPOL and TEMPONE, the pH-sensitive probe ATI and spin-labeled biologically active substances diclofenac, dihydroquercetin, tocopherol, and ibuprofen. The influence of parameters of the supercritical process, including time of pressure release, on the structure of the matrices and the uniformity of distribution of the paramagnetic substance will be analyzed. The comparative analysis of the release kinetics for various dopants in vitro will be carried out. The rate of release will be compared with the changes occurring within the polymer material during its swelling and hydrolysis.

This work was supported by the Russian Foundation for Basic Research (grants 17-02-00445 and 18-29-06059).
Current trends in tissue engineering are directed to ecologisation of the manufacturing process. Therefore, supercritical fluid technologies attract major attention in scientific and clinical societies. The key tool in this technology is supercritical carbon dioxide (scCO$_2$) that meets the criteria of biosafety and efficiency when used as a medium for preparation of tissue-engineered constructs, sterilization of medical devices, decellularization of mammalian tissues and impregnation of biomaterials with biologically active compounds. Relatively low critical temperature (31.1 °C) and pressure (7.38 MPa) allow performing the extraction avoiding the destruction of the material being processed. This allows to work with thermosensitive polymers, such as collagen and other proteins of extracellular matrix. Besides adjusting the parameters of scCO$_2$ extraction for each particular task, one can personalize the properties of final products.

The key features of the biomaterial fabrication and modification in scCO$_2$ medium will be illustrated with particular focus on the production of decellularized transplants of mammalian tissues with personalized biomechanics.

Acknowledgements. This work is supported by the Russian Science Foundation (Grant No. 18-15-00401) and Russian Foundation of Basic Research (grant No. 18-33-00982).
ONE-STEP SYNTHESIS OF ORGANOSILICON AEROGELS, THEIR PROPERTIES AND PROSPECTS.

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Aerogels — gels in which the liquid phase is completely replaced by gas — are materials of very low density — from 0.4 to 0.01 g/cm³. Because of this, they have a low thermal conductivity from 0.05 to 0.01 W/m*K and a high specific surface area (300-1500 m²/g). Because of these properties aerogels have been used as insulating materials¹, supports for heterogeneous catalysts², sorbents³.

While aerogels based on C, SiO₂, Al₂O₃ and other metal oxides have very low density and thermal conductivity⁴, their mechanical, hydrophobic, and sorption properties do not always meet the requirements of modern science and technology. In this regard, active research is being conducted to obtain flexible hydrophobic aerogels that can sorb not only hydrophilic, but also hydrophobic organic compounds, for example, oil from the surface of a polluted reservoir. To obtain such aerogels an organic-inorganic hybrid network (for example, MeSiO₁.₅) is used instead of a fully inorganic one (SiO₂, Al₂O₃, ZrO₂).

The most common method of obtaining aerogel consists of 2 steps: fabrication of the gel in an organic solvent using a sol-gel method and further solvent removal by drying in supercritical CO₂ (scCO₂).

Alternative solvent removal methods include freeze drying², drying at atmospheric pressure³, vacuum drying⁵, sublimation of the organic solvent⁶. Each of them has its advantages and disadvantages. However, regardless of the method, the need for drying makes the process multi-step.
There is also a one-step method of producing aerogels, when aerogel is formed directly in the scCO₂ media. Hydrosilylation\(^7\) and hydrothiolation\(^8\) reactions can be used for this method. Three-dimension network formation is very fast that allows to reduce the preparation time to 1-4 hours.

The mechanical, hydrophobic, and sorption properties of such aerogels strongly depend on the parameters of the initial precursors and synthesis conditions — temperature, pressure, scCO₂ density, and the presence of a co-solvent. Due to this, it is possible to obtain aerogels with specified properties, the choice of which depends on specific tasks.

One-stage synthesis of aerogels is promising direction for both fundamental and applied science. In this regard, the talk will focus on this approach.

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HYBRID AEROGELS: PROPERTIES, MANUFACTURING, TRANSFER TO INDUSTRY

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Hybrid aerogels are new promising functional composite materials. The development of the scientific foundations of technologies for their production, the study of physicochemical, mechanical, and biological properties are urgent tasks. In D. Mendeleev University of Chemical Technology of Russia work is underway on obtaining aerogels to create structural materials – heat-insulating materials based on silica and a fibrous substrate; metal oxide aerogels with record low thermal conductivity values below 0.017 mW/m*K, non-combustible, used at high and low temperatures in rocket and aircraft construction, homes and clothing for the Arctic. Aerogels are developed as functional materials: organic and inorganic aerogels with nanotubes, silica-resorcinol-formaldehyde aerogels. Their purpose is filtration, sorption, gas separation, sensors for industrial and toxic gases. The conducted studies allowed to establish the possibility of using these aerogels as sensors (response time is less than 2 minutes when MPC is exceeded for a series of industrial gases), as filters for airplanes, trains, and sorbents of water vapor in industrial and household appliances (with multiple recovery).

Much attention is paid to the development of hybrid aerogels from natural biopolymers – chitosan, sodium alginate, cellulose – for medical purposes, pharmaceuticals and regenerative medicine. These are sorbents, sponges for medicine; delivery systems of hardly soluble active pharmaceutical ingredients when creating new compositions; these are collagen-based bone tissues and various scaffolds for cell growth (for example, «artificial skin»).

In addition to experimental research, multilevel mathematical and computer modeling, scaling and design are being developed. Calculated installations with
working volumes 30, 70, 100, 500 liters. As part of an agreement with the Ministry of Industry and Trade of the Russian Federation, a technology is currently being transferred for the production of composite insulation materials based on aerogels from domestic raw materials.
According to the report [1], over more than 40 years of operation, the Baikal Pulp and Paper Mill has accumulated more than 6.2 mln tons of waste, including 2.6 mln tons of sludge-lignin. The bulk of sludge-lignin is stored at the Solzansky waste landfill, located on the shore of Lake Baikal. The sludge-lignin is composed of the following components (wt%): lignin 50–53, activated sludge 15–25, alumina 5–10, polyacrylamide 5, and cellulose fibre 5. The presence of polychlorodibenzodioxins and polychlorodibenzofurans in sludge-lignin [2], whose source is the chlorination of organic compounds in the bleaching of cellulose, is of particular concern. Based on the results of long-term observations, the authors [2] note that during the storage of sludge-lignin, dioxins were chemically transformed that resulted in an increase in the proportion of polychlorodibenzodioxins by almost 30%, mainly due to the formation of 2,3,7,8-tetrachlorodibenzodioxin.

Despite the fact that the sumps of the Solzansky waste landfill are earthquake-resistant and have a multilayer hydro-proofing, consisting of natural and synthetic materials that prevent drainage, a threat of pollution of Lake Baikal still exists in the event of destruction of waste storage in consequence of dangerous geological processes such as earthquakes and mudflows. To eliminate the threat to the unique ecological system of Lake Baikal, it is necessary to develop environmentally friendly waste management technology with regard to pollutions of the Baikal Pulp and Paper Mill. The difficulties of processing sludge-lignin are due to its complex chemical and dispersed composition, as well as a high water-bearing nature. Proposed methods of sludge-lignin disposal, such as grouting with the addition of lime, fly ash from coal combustion and/or gypsum, electro-osmosis, treatment with iron salts and freezing of moisture have not found practical application because they do not solve the problem.
The research results on gasification and oxidation of sludge-lignin in the flow of supercritical water and water-oxygen fluid at uniform heating of the tubular reactor to 923 and 733 K, respectively, are presented. The sample of sludge-lignin was taken at Sump #2 of the Solzansky waste landfill. The investigated sample is characterized by water content 91.1%, ash content per dry basis 22.5%, and has a high content (wt.%) of aluminum 8.2, sulfur 2.8, nitrogen 2.7, chlorine 1.3, phosphorous 0.6, and iron 0.5. From the results of mass spectrometric analysis, it follows that the highest yield of \( \text{H}_2\text{S} \) formed via the thermolysis of aliphatic \( \text{S}−\text{C} \) bonds occurs at 668−713 K. A high content of formaldehyde was detected in the composition of volatile products obtained at \( T \leq 713 \) K. The yield of \( \text{H}_2 \) generated through the water gas shift and steam reforming reactions increases at \( T > 713 \) K. The maximum yield of liquid products, including phenols, is observed at 473−623 K. It is shown that in consequence of sludge-lignin gasification, a carbonised residue with a high specific surface is formed.

Based on time dependences of the reactor wall temperature and power of the resistive heaters during sludge-lignin oxidation in the \( \text{H}_2\text{O}/\text{O}_2 \) mixture, it was revealed that the process begins at 440 K, and the maximum rate is realized at 583−643 K. From the comparison of sludge-lignin oxidation in an air medium (thermogravimetric analysis) and in the \( \text{H}_2\text{O}/\text{O}_2 \) mixture, it follows that in the latter case, the oxidation completes at a temperature by \( \approx 200 \) K lower. Based on the mass spectrometric analysis data, the temperature dependence of degree of carbon removal as part of \( \text{CO}_2 \) and \( \text{CO} \) from sludge-lignin is obtained. The liquid products composition was studied with the use of ultimate analysis and IR spectroscopy. The composition of mineral components was determined by means of X-ray diffraction analysis, atomic absorption and X-ray fluorescence spectroscopy. It is shown that \( \text{Al}_2\text{O}_3 \), \( \text{Fe}_2\text{O}_3 \), \( \text{SiO}_2 \), \( \text{AlPO}_4 \), and \( \text{CaSO}_4 \) are the main components of sludge-lignin mineral conversion residue. It is revealed that the simultaneous formation of \( \text{HCl} \) and \( \text{H}_2\text{SO}_4 \) during oxidation of chlorine- and sulfur-containing organic substances results in corrosion of stainless steel.

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SYNTHESIS OF NITROCOMPOUNDS IN 1,1,1,2-TETRAFLUOROETHANE MEDIUM

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Efficient methods for nitroesters and nitramines synthesis by the nitration of corresponding alcohols, amines and their derivatives with dinitrogen pentoxide in a liquid 1,1,1,2-tetrafluoroethane (TFE, Freon R134a) under batch and continuous flow conditions have been developed.

The use of TFE as a reaction medium reduces fire and explosion hazards of the nitration processes due to its non-flammability, thermally stability and a high heat capacity ($C_p = 1.40 \text{ J} \cdot \text{g}^{-1} \cdot \text{K}^{-1}$ at 0.57 MPa and 20 °C). Moreover, a low TFE vapor pressure (0.57 MPa and 20 °C) allows solvent recycling with simple and available laboratory equipment which makes the proposed synthesis of nitro compounds environment-friendly.

The work was financially supported by the Russian Science Foundation (projects 18-73-10207).

VAPOUR-LIQUID EQUILIBRIUM OF ACETONE-CO$_2$ MIXTURES OF DIFFERENT COMPOSITIONS AT THE VICINITY OF THE CRITICAL POINT

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Abstract

The vapour-liquid equilibrium of acetone-CO$_2$ mixtures is studied by computer simulation at 11 different compositions, ranging from neat CO$_2$ to neat acetone, in a 50-100 K wide range of temperatures at the vicinity of the critical point. The composition dependence of the critical parameters is determined, for the first time, in the entire composition range. It is found that while the critical temperature changes monotonically with the composition, the critical pressure goes through a maximum around the acetone mole fraction value of 0.3, and the critical density might also exhibit a maximum in the acetone mole fraction range of 0-0.2. Temperature dependence of the surface tension is also determined in the entire composition range. The obtained results agree, in general, well with experimental data; their deviation remains below the range within which different experimental data sets deviate from each other. Since experimental data in this respect exist, unfortunately, only in limited ranges of compositions (at low acetone mole fractions) and temperatures (data above about 335 K are scarce), the present study largely extends the range of thermodynamic conditions in which we have reliable information on the liquid-vapour equilibrium and critical conditions of acetone-CO$_2$ mixtures.
SCF FORMATION OF COMPONENTS OF PROLONGED ACTION ANTIBACTERIAL DOSAGE FORMS

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Currently, there is an increase in the disease of multidrug-resistant tuberculosis, whose therapy can last up to two years. Therefore, the development of new dosage forms, allow reducing both the toxicity of the drugs contained in them, and the frequency of their introduction is extremely important. One of the most promising approaches to the creation of such forms is the development of bioresorbable systems with drugs encapsulated in them, capable of providing targeted delivery and localization of the latter in target organs with their subsequent prolonged release and effect. The aim of the work was to develop components of dosage forms of prolonged action based on polylactoglycolide (PLG) scaffolds and microparticles and antibiotics, levofloxacin (LFC) and gentamicin (GMC) using the basic principles of modern supercritical fluid (SCF) technologies that eliminate the use of toxic solvents and the use of high temperatures.

Preliminary studies of solubility in sc-CO₂ and the possibility of micronization of the original pharmaceutical preparations using the RESS method carried out to select and optimize the conditions of SCF encapsulation of GMC and LFC in bioresorbable polymer scaffolds and microparticles.

The study of the solubility of GMC in supercritical carbon dioxide (sc-CO₂), carried out by the method of IR Fourier spectroscopy at pressures up to 20 MPa and temperatures up to 60 °C, as well as scanning electron microscopy before and after SCF processing, showed that GMC is practically insoluble sc-CO₂ under these conditions. The sensitivity of the used spectroscopic measurement method (of the
order of 10–5 molar fractions) was not enough for the quantitative measurement of the LFC solubility. Accordingly, micronization of LFC and GMC by the RESS method was ineffective. Therefore, their mechanical grinding with an agate mortar was used to reduce the size of the original drug substances (from 50 ÷ 200 μm to 5 ÷ 20 μm) before their SCF encapsulation in polymer structures.

Antibiotics (10 wt.%) were encapsulated into the PLG microparticles and scaffolds using the methods of PGSS and SCF plasticization and subsequent foaming in sc-CO₂. Plasticization of the polymer carried out in sc-CO₂ for 1 hour at temperature of 40°C and pressure from 10 to 20 MPa during the formation of both microparticles and PLG scaffolds. The formed microparticles had a characteristic size of 5–20 μm, and the scaffolds were cylinders 5 mm high and 5 mm in diameter.

The study of kinetics of GMC and LFC release from the formed polymeric structures into phosphate-saline buffer solution carried out using the methods of Raman spectroscopy and UV-spectrophotometry. The change in the concentration of GMC and LFC in the solution measured at regular intervals. The initial release (“burst”) for LFC was to about 75% of the total amount of encapsulated LFC in experiments with PLG microparticles for the first day. Then, by 4 days, its output was 100%. At the same time, the GMC almost completely discharged during the first day of the experiment. On the contrary, the initial release of LFC was 4-6% per day, and the GMC was 28% in the case of PLG scaffolds. Further, the release of drugs occurred almost linearly. 90% of the GMC released into the solution by 15 days, and LFC by 27 days of the experiment.

Investigation of the effect of released antibiotics on the growth dynamics of the M.tuberculosis H37Rv laboratory strain in vitro demonstrated an increase in the growth delay of cultures with controlled accumulation of antibiotics released from polymers in the growth medium.

Thus, by means of SCF technologies, levofloxacin and gentamicin were encapsulated in polylactoglycolide scaffolds and microparticles. It has been shown that the use of SCF methods allows to control the size, shape and morphology of formed structures and, accordingly, the rate of release of antibiotics into model environments, and to control the growth of mycobacterium tuberculosis. In our opinion, such approach can
be considered as very promising for the development of new highly effective anti-tuberculosis dosage forms of prolonged action.

This work was supported by the Ministry of Science and High Education within the State assignment FSRC “Crystallography and Photonics” RAS in part of the development of SCF methods for the formation of bioactive scaffolds, within the State assignment CTRI in part of in vitro studies and RFBR (No. 18-29-06062 microns) in parts of the development of prolonged action dosage forms.
OR-2

SUPERCritical CO₂ AT CARTilage DECELLularization

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The creation of injectable forms of cell-engineered structures for the stimulation of regeneration processes in damaged organs is based on the cultivation of cells on matrices consisting of micro particles among which tissue-specific matrices obtained from decellularized tissues are of particular interest and provide a microenvironment for cells similar to the native extracellular matrix. Among the existing methods of decellularization of both whole organs and their fragments, ionic detergents are most often used. However, the decellularization of dense cartilage tissue under the influence of detergents occurs only to a small extent.

The aim of this work was to prove the possibility to obtain a tissue-specific decellularized matrix from micro particles (MP) of pig cartilage by consecutive treatment of MP by detergents and supercritical CO₂.

Materials and methods

Samples of porcine cartilage MP of 30-100 µm sizes were ground by cryomill (Retch, Germany) at −196°C. MP was decellularized at room temperature and periodic mixing by magnetic stirrer (3 times a day for 1 hour) in 3 shifts of phosphate-saline buffer (BioVitrum, Russia, pH = 7.4), containing 0.1% sodium dodecyl sulfate (“Sigma-Aldrich”, USA) and increasing concentration (1, 2 and 3%) of Triton X100 (“Sigma-Aldrich”, USA). MP treatment in a supercritical CO₂ (sc-CO₂) atmosphere was carried out at a pressure of 150-300 bar, T = 35°C, with a flow rate of sc-CO₂ of 2.5±0.5 ml / min for 8-24 hours using RESS-SAS equipment (“Waters corporation”, USA). Ethanol (96%) at a concentration of 5-10% was used
as a polarity modifier. The degree of decellularization of MP was assessed by histological methods (stained by hematoxylin and eosin) and by detection of the residual amount of DNA in the samples using DNA-binding fluorescent dye DAPI (Sigma, United States).

**Results and discussion**

The effect of the order of the sequence of detergents and sc-CO$_2$ on the effectiveness of decellularization of pig MDC cartilage was studied. In the case of treatment with detergents after sc-CO$_2$, the required degree of decellularization of MP was not achieved. Histological analysis of the samples showed that only a partial release of chondrocytes from the lacunae (structural formations in the cartilage tissue) occurs, as a result of which in some microgranules cells free from cell areas are found, but cells integrity remains. An increase in processing time from 8 to 24 hours is accompanied by an increase in the number and size of MP areas free from cells due to their exit from the lacunae, but even in this case the destruction of chondrocytes does not occur. The introduction of 10% ethanol as a polarity modifier leads to the destruction of part of the chondrocytes directly in the gaps, but the number of lysed cells is insignificant, so additional research with the DAPI dye was considered impractical. Treatment MP by detergents followed by sc-CO$_2$ is effective at a pressure of 300 bar. In the histological preparation of MP cartilage non-disrupted cells were almost completely absent. A study with the DAPI dye showed that depending on the choice of treatment mode from 50 to 90% of MDC samples of cartilage were completely free of DNA or contained only single whole cells. However the macro and microstructure of an essential part of the decellularized MDC cartilage undergo significant changes: fibrillation, tearing and fragmentation of particles are observed. The introduction of ethanol assists to reduce the severity of such changes. It can be assumed that finding the optimal pressure in the range of 150–300 bar and the processing time in the range of 8–24 hours, followed by processing with DNase will allow reaching complete decellularization of MP while maintaining the native structure of cartilage.
**Conclusion**

To achieve the highest possible degree of decellularization, the treatment of MP cartilage should be carried out first with detergent solutions followed by exposure to sc-CO₂ at a pressure of 300 bar. The introduction of a polarity modifier (ethanol) at a concentration of 10% has a positive effect both on the degree of decellularization and on the character of the fibrillation of the particles of the tissue-specific decellularized matrix.

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OR-3

THE FEATURES OF POLYMER SYNTHESIS IN SUPERCRITICAL CARBON DIOXIDE

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The advantages of supercritical carbon dioxide as a solvent and the features of this fluid as a medium for different methods of polymer synthesis are discussed in the presented report.

For radical polymerization in SC CO\(_2\): dissolution questions, initiator activity, specific polymer properties, on example of Polyacrylonitrile;
for anionic polymerization: inhibitory properties of SC CO\(_2\), polymerization possibility, competition for active center, on ethyl-\(\alpha\)-cyanoacrylate example;
for coordinative-ionic polymerization: molar relation of monomers and a transition in to supercritical state, polymerization specifications in comparison with organic solvents, phase transition and structure of main chain, carbonization of active centres, a pressure as a control factor of monomers conversion degree, alkylene oxide is a monomer and a solvent, on polycarbonates and their terpolymers examples;
for polycondensation: dissolution problems, polymers synthesized and the INEOS contribution, SC CO\(_2\) as a catalyst, heterogeneity questions and methods of limitations by molecular mass overcoming, SC CO\(_2\) plasticizing effect and its influence on decrease of polymer T\(_g\) and T\(_{\text{melt}}\) depression of monomers, on aromatic polyimides, polyarylates and another polymers synthesis examples.
The results of studies of the photoactive polymer systems formation with photochromic, luminoform and sensitizing properties in supercritical carbon dioxide (ck-CO₂) are presented. The main feature of such processes is the ability of carbon dioxide in a supercritical state to penetrate into the volume of the polymer, creating in the matrix, in addition to existing under normal conditions, new areas of "free volume", and almost completely removed after the end of the SCF-impregnation process. This enables the direct participation of carrier macromolecular fragments in the formation of donor-acceptor complexes with functional groups of photoactive compounds (FAS) administered and the achievement of a certain conformational chemical correspondence between the introduced FAS and individual structural fragments of the polymer matrix. In particular, the formation of such stable conformational structures was observed during GFR impregnation of polymers of different chemical structures with photochromic compounds while stabilizing flat colored forms of photochromes that are thermodynamically unstable under normal conditions, but sterically more advantageous than non-planar initial forms. At the same time, the input concentrations of photochromic compounds, as well as the functional characteristics of the compounds formed, including the lifetime in the excited state, depended on the structure of the polymer matrix and the spiro compound, the degree of swelling of the polymer matrix in ck-CO₂, and the modes of impregnation. The use of co-solvents and some chemical additives capable of forming weakly bound complexes with FAS, leading to an increase in the size of the “free volume” areas in the polymer available for conformational rearrangements in
the structure of the FAS under excitation and relaxation, opens up new possibilities for directional changes in the functional characteristics of the resulting composites. The peculiarities of the formation of compositions with luminoform and photosensitizing properties in the medium of ck-CO$_2$ will also be considered.

The work was performed as part of a state assignment (theme V. 46.14, No. 0082-2014-0006) and with the support of the Russian Foundation for Basic Research (grant 18-29060-019 mk).
OR-5

FIXATION OF BIOACTIVE SUBSTANCES USING POLYLACTIDE ON
THE SURFACE OF THE BONE MATRIX
IN THE ENVIRONMENT SCF-CO₂

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The ability of the L/D isomer of polylactide, viscosity of 0.2 cm³/g, mass of 30 kDa in supercritical carbon dioxide to create a thin film on the porous surface of highly purified xenogenic bone matrix with the aim of fixing pre-applied bioactive substances on it, to create implantable bioengineering structures with a slow release of the active ingredient. Electron microscopy images were taken of the material with the film. The result was a material with an antimicrobial drug. During the experiment, the in vitro yield of the drug was observed for a month, which is a good indicator for the use of the product obtained in this way as an implant material with a dosage form of a metered yield.

Keywords: polylactide, supercritical carbon dioxide, xenogenous bone matrix, bioactive substances, metered yield
OR-6

USING scCO$_2$ TO CREATE POLYMERIC PARTICLES FOR SELECTIVE LASER SINTERING

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The focus of this research is to produce novel polymers for selective laser sintering (SLS) 3D printing via dispersion polymerisation in supercritical CO$_2$ (scCO$_2$). Dispersion polymerisation is ideal because it creates discrete spherical particles in the 0.1 to 10 micron size range.$^1$ We have used methyl methacrylate monomer, the initiator is azobisisobutyronitrile (AIBN) and a monomethacrylate terminated poly(dimethylsiloxane) (PDMS-MA) as the stabiliser dissolved in the scCO$_2$. The particle sizes range from 0.5 to 5 microns – below (Fig.1) are shown PMMA particles of a size of 0.6 microns.$^2$

![Fig.1. PMMA particles formed from dispersion polymerisation in scCO$_2$.](image)

Such polymeric particles could be used to develop high (ca. 10 µm) resolution SLS 3D printing. We have created a range of functionalised polymeric particles, with the aim of introducing colour or enhancing mechanical strength.
Particles were functionalised by creating a polymeric shell on the outside of each sphere containing either double bonds or dye molecules. The purpose of the double bonds was to provide a means of producing in-situ or post printing chemical bonding, to increase the mechanical properties of the parts. Double bonds were produced by incorporation of an asymmetrical divinyl monomer (allyl methacrylate (AMA)) in a random copolymer with MMA, RAFT control was employed to retard crosslinking of the polymer. Polymeric dyes provide the best route for colouration of the particles, with good control over the thermal properties and flow behaviour of the colourant. As of this moment red and yellow dyes have been successfully incorporated into polymers and polymeric particles.

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References:
CONDUCTING NMR EXPERIMENTS AT SUPERCritical PARAMETERS OF STATE

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NMR spectroscopy is an indispensable method for analyzing the structure and dynamics of molecules in liquids. Modern NMR approaches allow obtaining direct information about the geometrical configuration of molecules in liquids, which is very important when solving problems of modern physical chemistry of fluids. However, the NMR method is extremely problematic when it touches upon experiments at pressures above 100 bar. This report presents the peculiarities of a high pressure NMR experiment, as well as the effect of the NMR cell on the resolution of the spectrometer. In addition, the latest results obtained using the unique molecular fluid spectroscopy instrumentation at G.A. Krestov Institute of Solution Chemistry will be presented and discussed together with the development vistas and possibilities of this method.

The experimental data were obtained using the molecular fluid spectroscopy facility of G.A. Krestov Institute of Solution Chemistry, RAS.

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EFFECT OF THE CHITOSAN IMPREGNATION CONDITIONS IN THE SC-CO₂ MEDIUM BY HYDROPHOBIC DIARYLIMIDAZOLES ON THE KINETICS OF THEIR RELEASE IN WATER PHASE

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One of the ways to improve the pharmacological properties of drugs and increase the duration of their action on the affected cells of the body is the creation of prolonged dosage forms. To date, the most common drugs of this type are "retard" dosage forms that is a polymer matrix, in which the active substance is distributed.

This work is devoted to determining the optimal conditions for creating of matrix compositions with a slow release of active substances and the study of their release kinetics from the matrix into the aqueous model medium with pH = 1.6. The created matrix compositions are based on chitosan and substituted diarylimidazoles (DAIs) - bis-4,5 (4-methoxyphenyl) -imidazole – MID (1) and bis-4,5 (3,4,5-trimethoxyphenyl) -imidazole – MID (2), which has an antitumor effect.

It is shown that the chitosan impregnation with DAI in sc-CO₂ medium proceeds more efficiently in the presence of a co-solvent — water. It has been found that there is an optimal value of the water content in the reactor, equal to 0.17% by vol., at which it is possible to introduce into the polymer matrix the largest amount of DAI (up to 2.6% by mass). In addition, it should be noted that the use of water in the impregnation process has an effect on the release kinetics of the scf-introduced DAI from the chitosan matrix into the aqueous medium with pH = 1.6, which simulates gastric juice. It turned out that the DAI release rate for chitosan-MID (1) samples does not depend on the presence of water in the scf-impregnation process, and in the case of chitosan-MID (2) samples, after their impregnation in the presence of water, the MID (2) release rate slows down significantly.

For the first time, it is shown that the solubilization of DAI molecules by Pluronic F-127 before their scf-introduction into the chitosan matrix leads to the disaggregation
of DAI molecules and the decrease of their subsequent release rate from the polymer matrix into the aqueous medium.

*This work was supported by the Russian Foundation for Basic Research: Grant no. 18-29-06019 mk (in part of obtaining matrix polymer systems in the sc-CO₂ medium) and Grant No. 18-33-00968 mol_a (in part of studying the kinetics of DAI release from chitosan matrices into the aqueous medium).*
LOW-COHERENCE REFLECTOMETRY OF THE STRUCTURE OF FOAMED POLYLACTIDE MATRICES

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Nowadays, a significant attention is paid to applied research of SCF-synthesis of highly porous foam-like materials [1-3]. However, it should be noted that there are no sounding results in the modeling of evolution of such structures at various stages of the synthesis. This is due to a variety of various processes in foamed polymers. Correspondingly, gathering of new empirical data related to features in formation of the structure of these materials is of significant interest.

In this work, we present the results of experimental study of the structure of SCF-foamed highly porous polymer matrices. These results were obtained using the method of low-coherence reflectometry (LCR), which is based on analysis of the diffusely reflected probe light. The LCR signal analysis is based on evaluation of the signal decay depending on the probe depth [4]. Figure 1 displays the dependences of the averaged normalized intensity of the LCR signal on the probe depth $I(z)$ for three different values of the initial pressure of carbon dioxide used for polylactide foaming.

![LCR signal analysis](image)

Fig. 1. Dependencies of the normalized LCR signal on the scan depth for synthesized polylactide matrices with the thickness equal to 2 mm. The temperature in the reactor was equal to 309.16 K.
The decay rate of the LCR signal is determined by the transport mean free path of light propagation in the medium, effective refractive index of the medium, and its geometrical thickness. The previously used technique for analyzing the LCR signals, which is based on estimations of the transport mean free path (and, accordingly, the characteristic pore size in the system) from the rate of exponential decay of the LCR signal [4], cannot be applied for characterization of the foamed polylactide matrices. A novel technique for determining the transport mean free path is based on the results of Monte Carlo simulation of the temporal response of studied systems in the region of crossover between two characteristic modes of the response decay. The simulation results are compared to the experimentally obtained normalized reflectometric signal at the scan depth equal to the geometric thickness of the sample. Thus, when comparing the results of experimental study with the modeling data, the non-monotonic behavior of the transport mean free path in synthesized structures was established for the case of quasi-adiabatic foaming; the transport mean free path strongly depends on the initial pressure of the plasticizing/foaming agent. The considered technique can be applied for choice of foaming modes, which provide required structural and functional properties of the synthesized porous materials.

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OR-10

LASER MICROSTRUCTURE OF TRANSPARENT OPTICAL MATERIALS IN THE MEDIUM OF SCF


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Technologies of micro- and nanostructuring of various materials are in demand practically in all branches of modern industry. A convenient tool for forming various micro and nanostructures is a laser. With the help of laser radiation, it is possible to distribute the energy according to a given space-time scenario and to carry out a controlled modification of the material. The phase state of the environment fundamentally affects the mechanisms of interaction of laser radiation with materials. Of particular interest is the study of laser modification of materials placed in the medium of supercritical carbon dioxide. Such an environment is a good solvent and, due to zero surface tension, is able to transport solutes into micro and nano pores of various materials or, conversely, to effectively clean materials from impurities. By varying the pressure and temperature, the specific density of the SCF can be varied over a wide range, which also distinguishes them from ordinary liquids. The combination of GFR and laser technology can open up fundamentally new possibilities for processing materials at the micro and nano levels.

The report will present the results of research on the laser formation of microstructures on the surface of leucosapphire and quartz in a medium of supercritical carbon dioxide. The results of the formation of microstructures with different topologies, formed by laser radiation of nanosecond and femtosecond pulse duration, will be presented.

The work was financially supported by the Russian Foundation for Basic Research (project 18-29-06056 in terms of developing methods for the microstructuring of optical materials in the medium of supercritical carbon dioxide) and the Ministry of Science and Higher Education as part of the work on the State task of the Federal Research Center "Crystallography and Photonics" of the Russian Academy of Sciences in terms of the development of laser technologies microstructured materials.
EPR SPECTROSCOPY OF SPIN PROBES IN SUPERCRITICAL CO$_2$

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Electron paramagnetic resonance (EPR) spectroscopy is widely applied in the study of polymeric and biological systems. Due to the fact that paramagnetic particles are rarely found in nature, so-called spin probes or labels (spin probes chemically bonded to the polymer under study or doping molecules) are often introduced into the system under study. These are usually paramagnetic particles that are stable under experimental conditions, for example, nitroxyl radicals. The EPR allows one to determine the nature of the spin probe environment, for example, the local polarity and the pH of the medium around the spin probe, to study the spin probe mobility (translational and rotational diffusion coefficients), to identify the local concentration. The first part of the paper will give a brief overview of the use of EPR spectroscopy in the study of supercritical fluids.

The second part of the report will be devoted to the authors' work on the study of the swelling of polymer systems in supercritical (sc) CO$_2$ and the determination of the diffusion rates of spin probes in scCO$_2$ and polymer-scCO$_2$ systems. Using the original system for recording the EPR spectra of solutions in supercritical fluids, we determined the translational diffusion coefficients of the TEMPONE spin probe (4-oxo-2,2,6,6-tetramethylpiperidin-1-oxyl, 4-oxo-TEMPO) in scCO$_2$, and also in scCO$_2$-polylactide and scCO$_2$-polycarbonate systems. The TEMPONE spin probe diffusion coefficients in scCO$_2$ calculated on the basis of the EPR data are in good agreement with the diffusion coefficients of molecules of similar size, which are known from the literature and determined by other methods.

The research is supported by RFBR (grants № 17-02-00445 and 18-29-06059).
CONTROL OF MORPHOLOGY AND CRYSTALLINITY DEGREE OF PARTICLES OBTAINED VIA SUPERCRITICAL ANTI-SOLVENT PRECIPITATION

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A variety of process parameters in Supercritical Anti-Solvent (SAS) method potentially gives a possibility to obtain tailored particles with controlled morphology, crystallinity degree and particle size distribution. On the other hand, a variety of SAS parameters and their interrelatedness determine process complexity and weak predictability of result. Deep understanding of precipitation mechanisms and their influence on product characteristics is necessary for full-blooded use of SAS potential.

The aim of this work was the investigation of influence of SAS parameters on size, morphology and crystallinity degree of precipitated particles. Special attention was payed to thermodynamic factors, such as phase equilibrium, solubility in solvent – antisolvent – solute system etc.

Salbutamol sulphate, arbidol, fluoroquinolones and dicarboxylic acids were chosen as model compounds. It is shown, that change of morphology associated with concentration in initial solution change is possible for crystalline substances, contrary to amorphous substances. Supersaturation degrees in SAS process were calculated using developed method for measuring solubility in supercritical fluids using combination of SAS and supercritical fluid chromatography. Obtained data allow qualitatively predicting size and morphology of particles precipitated by SAS.

It is demonstrated, that phase composition of solvent – antisolvent – solute mixture can influence crystallinity degree of obtained particles. Amorphous particles are typical for single-phase regime and crystalline – for two-phase regime. It is shown
that solute can significantly shift mixture critical loci to higher pressure in comparison with critical loci of solvent – antisolvent mixture.

The work was financially supported by Russian Foundation for Basic Research, grant 17-03-01134. The part of work associated with salbutamol micronization was supported by Ministry of Education and Science of Russian Federation, project No. 03.G25.31.0273.
FORMATION FEATURES OF DIFFERENT LIGAND COMPLEXES OF RARE-EARTH ELEMENTS IN POLYMERIC MATRICES IN THE SUPERCRITICAL CARBON DIOXIDE CONDITIONS

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In this paper, fluorescent systems based on Neodymium (III) β-diketonate (Nd(Acac)_3), phenanthroline and polymers were obtained by impregnation in supercritical carbon dioxide (SC-CO_2). The used neodymium complex is well soluble in SC-CO_2, and the high diffusion rate of CO_2 molecules and the ability of polymers to swell in SC-environment allow using this method to obtain lanthanide-containing fluorophore polymers.

The samples of polymers containing Nd(Acac)_3, as well as Nd(Acac)_3 with phenanthroline (Phen) were obtained by impregnation in the SC medium. Oligourethanemethacrylate (OUM-5), polycarbonate (PC) and fluoroplastic (F-42) polymers were used in the form of optically transparent films (thickness <1 mm). Impregnation was being carried out in supercritical CO_2 at a temperature of 90 °C and a pressure of 180 bar for 1 hour. The fluorescence spectra of impregnated polymers were recorded, the type of which depends on the nature of the matrix. With the sequential introduction of Nd(Acac)_3 and phenanthroline molecules into OUM-5 and F-42 polymers, a bathochromic shift of the fluorescence maxima of the resulting systems is observed (up to 147 and 116 nm, respectively) (no shift of the bands in the PC spectrum was recorded). This probably indicates the process of formation of a new mixed-ligand Nd(Acac)_3/Phen/polymer complex, which passed directly inside the polymer matrix in the SC medium. It was shown that the magnitude of the shifts is influenced by the order of impregnation of polymers. Thus, the greatest shift in fluorescence bands was noted for the Nd(Acac)_3/polymer systems, followed by the introduction of phenanthroline into it. Such changes in the fluorescence spectra of impregnated polymers may indicate a different structure of the ligand environment of
the Nd (III) atom. This is probably the reason for the changes in the mechanisms of thermo-oxidative destruction of polymers impregnated by Nd(Acac)$_3$ and phenanthroline molecules, depending on the sequence of the introduction of such components.

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SOME ASPECTS OF CHIRAL PREPARATIVE SEPARATION

2 - TRET - BUTYLAMINO - 1 - (4 – OXI – 3 - OXIMETHYLPHENYL) – ETHANOL

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The need for effective preparative chiral separation methods for pharmaceutical substances increases significantly.

Chiral chromatographic methods for the enantiomeric separation of 1,2-ethanolamine derivatives are studied in various aspects. Analytical use of HPLC for the separation of enantiomers of the β2-adrenomimetic group - substituted 1,2-ethanolamines (salbutamol, salmeterol, etc.) has been described. For preparative purposes, the separation of enantiomers on a semi-industrial and industrial scale practically does not carry out the HPLC method.

Chiral chromatographic separation of enantiomers of substituted 1,2-ethanolamines by supercritical fluid chromatography (SFC) is a type of HPLC, the most promising. The special properties of supercritical fluids (high diffusion coefficient, low viscosity, good dissolving ability) increase the separation efficiency. The main advantage of SFC for the separation and purification of pharmaceutical substances is the elimination of large volumes of organic solvents. This is one of the serious prerequisites for the need to develop preparative separation of enantiomers of substituted 1,2-ethanolamines by SFC method.

We have also shown that the effectiveness of preparative chromatographic separation does not depend on the flow rate of the fluid, and with increasing mass flow rate of the fluid, the separation time decreases, which is due to the insignificant viscosity of the mobile phase in SFC.
Thus, it was found that when the mass flow rate of CO\(_2\) is ≤140 g/min, there is a sharp increase in the retention time of analytes (table 1), while the enantiomeric purity remains almost unchanged. This can lead to a significant decrease in the performance of the chromatographic system and the waste of CO\(_2\) and co-solvent (methanol), and the use of a mass flow rate of CO\(_2\) of more than 200 g/min is impossible due to the design and technical features of the preparative supercritical fluid chromatographic system.

Table 1. Characteristics of the preparative separation of 2-tert-butylamino-1-(4-hydroxy-3-hydroxymethylphenyl)-ethanol depending on the mass flow rate of the mobile phase (the volume of the introduced racemate sample for a single cycle is 0.85 ml; the co-solvent content (methanol) mobile phase - 18.0%; pressure - 120.0 bar)

<table>
<thead>
<tr>
<th>Mass flow rate of the mobile phase, g / min</th>
<th>The retention time of the S-isomer, min</th>
<th>The retention time of the R-isomer, min</th>
<th>The output of the R-isomer,%</th>
<th>Enantimeric purity,%</th>
</tr>
</thead>
<tbody>
<tr>
<td>140</td>
<td>3.4</td>
<td>3.8</td>
<td>32.8</td>
<td>91.60</td>
</tr>
<tr>
<td>160</td>
<td>3.0</td>
<td>3.3</td>
<td>33.2</td>
<td>91.47</td>
</tr>
<tr>
<td>180</td>
<td>2.6</td>
<td>2.9</td>
<td>33.5</td>
<td>90.80</td>
</tr>
<tr>
<td>200</td>
<td>2.3</td>
<td>2.6</td>
<td>33.7</td>
<td>91.26</td>
</tr>
</tbody>
</table>

A major problem in preparative SFC is the need to use large sample volumes with a high concentration of the separated substances.

The effectiveness of preparative separation is associated primarily with the sorption capacity of the column, which is determined by the ratio of the number of active centers of the sorbent and the number of analyte molecules.

The effect of the volume of the analyte solution of 2-tert-butylamino-1- (4-hydroxy-3-hydroxymethylphenyl) ethanol in methanol (86.0 g/l) on the effectiveness of preparative separation was studied (table 2).

Table 2. Characteristics of the preparative separation of 2-tert-butylamino-1-(4-hydroxy-3-hydroxymethylphenyl)-ethanol depending on the volume of an analyte sample in a single cycle (mobile phase mass flow rate 200 g/min; co-solvent content (methanol) in the mobile phase - 18.0%; pressure - 120.0 bar)

<table>
<thead>
<tr>
<th>Sample analyte, ml</th>
<th>The retention time of the S-isomer, min</th>
<th>The retention time of the R-isomer, min</th>
<th>The output of the R-isomer,%</th>
<th>Enantimeric purity,%</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.80</td>
<td>2.3</td>
<td>2.6</td>
<td>31.3</td>
<td>91.73</td>
</tr>
<tr>
<td>0.85</td>
<td>2.3</td>
<td>2.6</td>
<td>32.9</td>
<td>91.08</td>
</tr>
<tr>
<td>0.90</td>
<td>2.3</td>
<td>2.6</td>
<td>29.8</td>
<td>87.76</td>
</tr>
<tr>
<td>1.00</td>
<td>2.3</td>
<td>2.6</td>
<td>21.6</td>
<td>78.77</td>
</tr>
</tbody>
</table>
With an increase in the volume of the injected sample for a single cycle of more than 0.9 ml, the quality of separation deteriorates dramatically, which may be due to an excess of analyte molecules relative to the number of active sorbent centers, i.e. sorbate content in the sample of more than $0.3 \times 10^{-3}$ mol is higher than the sorption capacity of the column. When this happens, overload preparative chiral chromatographic column, which, in turn, reduces the selectivity of the separation and reduces the enantiomeric purity of the target product.

Thus, at this stage, we found that, firstly, with an increase in the flow rate of the mobile phase (mass flow), the retention time of analytes decreases, the difference in retention times of enantiomers and, accordingly, enantiomeric purity do not significantly change, which improves preparative chiral productivity chromatographic system; secondly, the performance of the preparative chiral chromatographic system is limited by the sorption capacity of the column, which determines the volume of a single sample of analytes.

_We are grateful to Altaivitamin CJSC for the opportunity to perform work on the Prep 200q SFC chromatographic system manufactured by Waters Corporation (USA)._
Aerogels are porous materials with high adsorption capacity, which makes it possible to successfully impregnate various substances into aerogels: active pharmaceutical ingredients, oils, additives for the food industry and many others. The purpose of this work is to study the process of obtaining spherical particles of organic aerogels based on egg protein for their further use in the food industry as carriers of various aromatic substances and food additives. Complex experimental studies were carried out, during which parameters of the process of obtaining aerogels based on egg protein were varied, namely, concentration of the initial protein solution and its pH. Based on the experimental data obtained, three concentrations and two pH values were selected at which stable gels were formed, which were then dried in supercritical carbon dioxide to form the finished material — aerogel. Analytical studies of the obtained aerogel samples were carried out, namely, the values of the specific surface area of the samples and their density were obtained, and scanning electron microscopy (SEM) images were obtained and provide low and high magnitude (Fig. 1).
It is shown that the obtained materials are very promising for their further use as carriers of aromatic substances and food additives. Thus, the next step in this work will be to investigate the process of impregnation the corresponding substances into the pores of aerogels based on egg protein. It can be concluded that spherical particles aerogels based on egg protein are of high interest for use in the food industry.
Application of unique properties of solvents in supercritical state at the stages of extraction and regeneration of the solvent in the process of solvent deasphalting (SDA) of heavy petroleum feedstock (HPF) makes it possible to significantly increase extraction and phase separation rates as well as to achieve high energy efficiency and reduce capital and operating costs compared to conventional processes [1, 2]. Despite this, the use of relatively high molecular weight and less selective solvents, such as n-pentane, which are most attractive for obtaining maximum amounts of deasphalted oil (DAO) and subsequent processing into components of motor fuels, results in the extraction to DAO not only resins, but also part of asphaltenes, that greatly deteriorates DAO quality. One of the promising ways to increase the efficiency of the supercritical SDA process is an addition to the system of highly dispersed sorption materials. The addition of small amounts of particles, especially nanoparticles, possessing a developed surface and high sorption activity with respect to the "binding" of asphaltenes and free organometallic compounds, to the HPF-solvent system can increase the degree of asphaltene and metal removal and improve the quality of DAO [3, 4].

This report presents the results of systematic studies of highly dispersed sorption materials (including those with magnetic properties) effect on the efficiency of deasphalting and demetallization of HPF using the solvent in the sub- and supercritical state. For the first time, in relation to the HPF upgrading under supercritical extraction conditions the synthesis of highly dispersed materials with desired properties, which have a high sorption capacity with respect to asphaltenes,
has been carried out. Effect of the type, properties and concentration of the adsorbents obtained as well as the methods of their introduction into the system on the efficiency of interaction with asphaltenes, DAO quality and SDA process indicators has been studied using the model solutions and real oil dispersed systems. In addition, the influence of the process conditions and the phase state of the solvent as well as the composition and properties of HPF (heavy oil, oil residues) and asphaltenes contained on upgrading efficiency has been determined.

The research results obtained will form the basis for the creation of the scientific foundations of high efficiency technology of supercritical extraction and upgrading of HPF. Reduction of the residual content of asphaltenes and metals in DAO at its high yields (at least 80%) will provide additional volumes of high-quality raw materials for further processing into components of motor fuels and base oils, thereby reducing the production of residual fuel oils and increasing the oil refining depth.

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**References**


OR-17

METAL OXIDE NANOPARTICLES AND AEROGELS OBTAINED IN A ONE-STEP PROCESS DIRECTLY IN SUPERCritical CO₂

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The interest in developing new methods for producing metal oxides is associated, in many ways, with the potential of these materials in the field of electrocatalysis — in particular, as an alternative to costly platinum-based catalysts [1]. For example, manganese oxides are known to successfully promote oxygen reduction reaction in an alkaline medium. Moreover, their electrocatalytic activity depends not only on the stoichiometry of oxides, but also on the type of crystal lattice and the morphology of the material [2]. Since these parameters are directly dependent on the method of production, the development of new methods for the synthesis of metal oxides is of both scientific and practical interest.

Both applications of heterogeneous catalysis and electrocatalytic applications require high porosity of catalytic materials. In this regard, the use of metal oxide aerogels is of particular interest. Often, the preparation of such materials requires multi-component and multi-step synthesis. In this paper, we present a new approach to obtaining both monodisperse nanoparticles of metal oxides and aerogels based on them in a single-step process directly in supercritical CO₂.

Nanoparticles and aerogels of metal oxides were obtained using thermal decomposition of organometallic metal precursors in solutions of supercritical CO₂. We used cyclopentadienyltricarbonyl manganese, manganese, iron, tungsten and cobalt carbonyls. It was shown that in the case of using cyclopentadienyltricarbonyl manganese, as a result of the synthesis, monodisperse nanoparticles are formed that possess electrocatalytic activity in the oxygen reduction reaction [3]. In the case of the use of metal carbonyls, as a result of the synthesis, porous structures are formed.
from the nanoparticles of the corresponding metal oxides with a specific surface area of up to 170 m²/g.

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HYBRID EXTRACTION TECHNOLOGIES IN SEPARATION PROCESSES

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Two-phase aqueous polymeric extraction systems, which are free of organic solvents and use cheap and ecologically friendly polymers such as polyethylene glycole, polyvinyl alcohol, polyvinylpyrrolidone are an attractive alternative to traditional extractants both from technological and ecological points of view [1]. These systems possess noticeable flexibility in extraction process management, allow many-fold concentration of both inorganic and organic target compounds from diluted water solutions. They are also totally chemically safe both for human and environment. Current central challenges in the progress of this extraction method include development of approaches for post-extraction isolation of target compounds from water-polymer solution as well as for polymer regeneration and recycling [2–5].

We proposed a hybrid extraction approach comprising extraction with an aqueous polymeric two-phase system and a consecutive treatment of an extract using supercritical fluid separation technologies. In order to study the ways of supercritical carbon dioxide applicability for fractionation of water-polymer solutions one has to employ a number of auxiliary physicochemical measurement techniques for the investigation of many-component mixtures under high pressure.

In this work, results are presented of the research on extractant composition choice and method development for the implementation of the proposed approach. A method was developed for the assessment of phase composition of a many-component mixture including supercritical CO₂. Also, a method for measuring distribution
coefficients of a substance in two-phase water-polymer-supercritical CO$_2$ systems was proposed.

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**References**


OR-19
EFFECT OF SWELLING IN SUPERCRITICAL CO$_2$ ON GAS SEPARATION PROPERTIES OF POLYMERS

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Amorphous glassy polymers are widely used as materials of gas separation membranes. However, the transport parameters of glassy polymers as non-equilibrium systems are affected not only by the chemical structure of the element, but also by the method of formation or subsequent treatment of polymer films or membranes. One of these methods of treatment, significantly changing the chain packing in the polymer matrix, is the swelling of polymers in supercritical CO$_2$ (sc-CO$_2$).

Modern experimental and computational methods for the study of amorphous glassy polymers indicate the microheterogeneity of their structure, which can be represented as a wide size distribution of micro-cavities (free volume elements) distributed in a more densely packed polymer matrix. The application of the microheterogenic model to the analysis of gas transport processes in glassy polymers shows that the level of permeability, diffusion and solubility of gases depends mainly on the average size of the free volume element, while the selectivity of gas separation is determined by the packing density and ordering of the chain packing in the dense phase of the polymer matrix. Recently the TIPS RAS has developed a method for quantifying the change in the chain packing ordering in amorphous glassy polymers, based on the analysis of gas diffusion coefficients [1].

In the present work, based on the data of the gas permeability method for polyhexafluoropropylene and some of polyetherimides, it is shown how the treatment of films in as affected by processing films in sc-CO$_2$ affects the density and ordering of the chain packing in the polymer matrix. It is shown that swelling in sc-CO$_2$ in all cases [1 – 3] leads to increase in the free volume and, consequently, to increase in gas...
permeability. However, in the case of polyetherrimides, the swelling in sc-CO₂ leads to additional ordering of the chain packing in the dense part of the polymer matrix and, consequently, to increase in the selectivity of the gas separation. Thus, treatment in sc-CO₂ allows to modify gas transport characteristics of amorphous membrane polymers.

**References**


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The report discusses approaches to the extraction and chemical modification of secondary plant metabolites in medium of subcritical water (SCW) [1] to obtain products with high added value from plant materials of the Russian Federation. Quercetin (QR), a plant polyphenol belonging to an extensive family of flavonoids, which have already found many applications in the pharmaceutical, food and cosmetic industries due to a wide range of their biological activity, is presented as a model compound of importance for the market.

QR demonstrates antioxidant properties, anticarcinogenic, cardioprotective, bacteriostatic, secretory properties, and also helps to reduce the growth of aging cells in vivo and serves as an effective senolysis agent [2]. The usual method of obtaining QR from the plant matrices (Fig. 1) includes two stages: 1) the extraction of rutin (RT) using the organic solvents and subsequent purification; 2) the hydrolysis of the obtained RT, for the isolation of QR.
As part of the development of low-cost and environmentally friendly methods for the preparation of QR, the authors studied the transformation processes of rutin to quercetin in the SCW. It was shown that the medium of subcritical water at 200-220°C provides a good yield of QR, comparable to the yield obtained by traditional acid hydrolysis. [3] The obtained result demonstrates the possibilities of using the SCW for processing plant materials, which are traditionally used to produce QR. As a source of rutin and quercetin, Sophora Japanese buds were used in the work (Fig. 1, Way 1). The possibilities of using the SCW medium for obtaining quercetin with a good yield using the one-step “one-pot” procedure (excluding the intermediate steps of extracting and cleaning RT-containing extracts) were studied (Fig. 1, Way 2).

It has been shown that high yields of quercetin are obtained by “one-pot” —the technique for a time is 13 times less than that required by using traditional procedures [4]. Thus, for the first time, a one-step “one-pot” procedure was developed for obtaining in a medium of subcritical water of importance to the market for natural antioxidant quercetin. The proposed method has the potential for the future development of low-cost and environmentally friendly technologies for the production of secondary metabolites for the pharmaceutical, food and cosmetic industries.

The evaluation of the possible applications of subcritical water and supercritical CO$_2$ demonstrated that in order to prevent technological lag in Russia in the field of chemical technology and pharmaceutical production, it is necessary to intensify research in one and the other direction. And if supercritical CO$_2$ is already a widely used technological tool today, then sub- and supercritical water is the toolkit of the nearest tomorrow.

**Acknowledgments**

This work was financially supported by the internal grant of the Southern Federal University (project no. VnGr-07/2017-04)

**Literature.**


A method for synthesizing various types of nanoparticles (nanorubins, quartz glass with ytterbium ions, silicon, bimetal particles) using pulsed laser ablation in the SC CO$_2$ environment with varying parameters of laser irradiation and supercritical media using multi-purpose experimental setup has been developed. A one-step method has been suggested to produce composites with metal nanoparticles formed by laser ablation using porous polymeric matrices of PTFE with different morphology as a substrate.

Experimental studies of thermoplasmonic laser induced wet etching of transparent materials in liquids, including churlish and superhard materials, have been carried out in sub- and supercritical water and CO$_2$. For the first time, a critical point has been approached by tuning both the static conditions (temperature and pressure in the reactor) and the dynamic local impact inspired by a focused laser pulse. The optimal range of laser radiation parameters for microstructuring of materials in liquids has been established.

A set of approaches for diagnostics of phase transitions in metal absorbing films have been developed using optical and acoustic methods. It has been shown that the
explosive boiling of water in a gel layer contacting with an absorbing film plays the key role in formation of microjets in laser printing with gel microdroplets.

A technology has been developed to create foam-like oriented luminescent structures in film samples of OPBI in the SC CO$_2$ using continuous laser radiation. We show foam-like structures obtained by synthesis of silver nanoparticles in polymer films performed by laser irradiation of the samples impregnated by a supercritical solution of a silver containing precursor.

Metal nanoparticles have been synthesized in the pores of transparent nanoporous 3D-matrices using laser irradiation at different wavelengths matching the plasmon resonances of the particles of different shapes. We show that the radiation wavelength affects such properties of the synthesized particles as shape and size as well as the plasmon band wavelength of the ensemble. A set of synthesis scenarios is proposed to obtain the ensembles of particles with different properties.

The techniques discussed here show potential to create a broad range of functional nanoporous materials involved in modern and future technologies of cleaning, catalysis, separate adsorption, storage and transportation of active substances, creation of optical and electronic devices, bio-implants, antibacterial therapy.

*The work was carried out with partial support from the RFBR grant 18-29-06056 MK.*
 CONDITIONS OF ANALYTICAL CHIRAL SEPARATION

1- (4-HYDROXY-3- (HYDROXIMETHYL) PHENYL) -2 - ((6- (1-METHYL-3-PHENYL-PROPHOXI) HEXIL) AMINO) ETHANOL


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The search and optimization of the conditions for selective chromatographic separation of a racemic mixture is a complex and time-consuming task; It consists of the following stages selection of a sorbent, co-solvent, composition of the mobile phase, dynamic modifier and its concentration in the mobile phase.

Sorbent selection is an important step in the chiral separation of the enantiomers of pharmaceutical substances. However, there are no a priori methods for choosing of a chiral sorbent for a specific task. For the chiral separation of 1,2-ethanolamine derivatives, they are used in both HPLC and SFC, columns with cellulose or amylose-based sorbents modified with phenylcarbamate substituents. The possibility of chiral separation of 1-(4-hydroxy-3-(hydroxymethyl) phenyl)-2-((6-(1-methyl-3-phenylpropoxy) hexyl) amino) ethanol (salmeterol) by SFC method on sorbents based on chemically grafted to silica (immobilized) amylose, with tris-3-chloro-5-methylphenylcarbamate (Chiralpak IG) and tris-3,5-dimethylphenylcarbamate (Chiralpak IA) substituents, and based on chemically grafted to silica gel (immobilized) cellulose, with tris 3,5-dimethylphenylcarbamate (Chiralpak IB) substituents. It was established that in the absence of a dynamic modifier, none of the sorbents exhibits selective sorption of enantiomers.

The addition of a dynamic modifier (triethylamine) allowed activating the sorption centers of the stationary phase based on tris-3,5-dimethylphenylcarbamate amylose (Chiralpak IA) and effecting the separation of the enantiomers of 1-(4-hydroxy-3-(hydroxymethyl) phenyl)-2-((6-(1-methyl-3-phenylpropoxy) hexyl) amino) ethanol.
We have shown that the selective separation of enantiomers is associated primarily with donor-acceptor interactions and the emergence of hydrogen bonds between the functional groups of the selector and analyte. The dynamic modifier increases the ability of the carbamate group of the selector to form hydrogen bonds. It was established experimentally that when the content of triethylamine 0.5 and 1% separation of salmeterol does not occur. Very low enantioselectivity was also observed when the content of 1.5% triethylamine in PF (Fig. 1).

![Separation of enantiomers of salmeterol base on a Chiralpak IA column. Separation conditions: PF CO2 / MeOH / Et3N. The share of co-solvent in PF is 20%. The proportion of Et3N in the cosolvent is 1.5%. Pressure 120 bar, temperature 32°C, flow rate 5 ml/min, salmeterol concentration in the sample solution 5 mg/ml, injected sample volume 10 μl (Investigator SFC System chromatographic system manufactured by Waters Corp.).](image)

Increasing the concentration of the dynamic modifier to 2.0-2.5% leads to an improvement in the selectivity of the separation of enantiomers (Figure 2), however, higher concentrations of the dynamic modifier do not affect the separation efficiency in any way.
Figure 2. Separation of enantiomers of salmeterol base on a Chiralpak IA column. Separation conditions: PF CO₂ / MeOH / Et₃N. The share of co-solvent in PF is 18%. The proportion of Et₃N in the cosolvent is 2%. The pressure was 120 bar, the temperature was 32°C, the flow rate was 3 ml min⁻¹, the concentration of salmeterol in the sample solution was 5 mg/ml, the volume of the injected sample was 10 μl (chromatographic system Investigator SFC System manufactured by Waters Corp.).

The effect of the co-solvent fraction in the mobile phase on the separation efficiency was studied. It is shown that with increasing methanol content in the mobile phase, retention times monotonously decrease, but the selectivity of separation also decreases (Table 1).

<table>
<thead>
<tr>
<th>c(MeOH), %</th>
<th>t₀, min</th>
<th>tᵢ₁, min</th>
<th>tᵢ₂, min</th>
<th>k₁</th>
<th>k₂</th>
<th>α</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>1,9</td>
<td>13,2</td>
<td>14</td>
<td>5,95</td>
<td>6,37</td>
<td>1,07</td>
</tr>
<tr>
<td>18</td>
<td>1,791</td>
<td>7,52</td>
<td>7,98</td>
<td>3,20</td>
<td>3,46</td>
<td>1,08</td>
</tr>
<tr>
<td>25</td>
<td>1,65</td>
<td>3,87</td>
<td>3,98</td>
<td>1,34</td>
<td>1,41</td>
<td>1,05</td>
</tr>
<tr>
<td>30</td>
<td>1,6</td>
<td>2,58</td>
<td>2,58</td>
<td>0,61</td>
<td>0,61</td>
<td>1</td>
</tr>
</tbody>
</table>

With a high content of methanol in the mobile phase, it, as a donor of hydrogen bonds, probably competes with analyte molecules in specific interactions with sorbent selector groups and prevents the separation of enantiomers. Thus, it was found that the optimal methanol content in the mobile phase, when separating salmeterol on Chiralpak IA sorbent, is 18%.

The effect of temperature and pressure on the selectivity of separation was studied and it was found that in the studied temperature range (25-35°C) and pressures (100-150 bar), these parameters do not affect the selectivity of separation.
Thus, we have experimentally found conditions for the enantioselective separation of 1-(4-hydroxy-3-(hydroxymethyl) phenyl)-2-((6-(1-methyl-3-phenylpropoxy) hexyl) amino) ethanol, optimization of the conditions requires further research.

*This work was supported by the RFBR grant №. 18-29-06033mk.*
DIRECTED SYNTHESIS OF CATALYST SUPPORTS BASED ON CRYSTALLINE SILICA IN SUB- AND SUPERCRITICAL WATER MEDIA AND CATALYTIC PERFORMANCE OF OXIDE COMPOSITES IN SELECTIVE OXIDATION OF LIGHT ALKANES

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Heterogeneous catalysts, as a rule, are composites that include components of different chemical nature and are characterized by a complex interaction between them. The key factors in achieving a high catalytic performance (activity, selectivity, durability, mechanical characteristics) are both the desired composition of the composite (chemical, phase), and the parameters of its "fine tuning": the particle sizes of the components, their spatial organization, structural and morphological features of systems at different levels (from atomic to macroscopic). To ensure the optimal combination of the above properties, detailed studies of the relationships between them and the methods of composite synthesis are required.

The object of study in this work is a mixed NaWMn-oxide catalyst, which is very efficient in the conversion of C₁-C₂ alkanes to ethylene. The optimum support for it is silicon oxide in the crystalline form of cristobalite. The system is formed in the course of high-temperature synthesis. When calcining precursor salts (for example, sodium tungstate and manganese nitrate) deposited on amorphous silica, it crystallizes to form a "network" of accreted cristobalite globules with deposited crystals (~ 1–5 µm) of Na₂WO₄ and Mn₂O₃ phases, and the formal specific surface area reduced from ~ 250 to units of square meters per gram. Sodium salts have a stimulating effect on the crystallization of SiO₂. Moreover, there is a possibility of modifying the carrier phase with ions of the active component, and if so, it becomes
unclear to what extent the catalytic properties of the deposited phases can be masked by catalysis on the modified carrier itself. This makes it difficult to interpret the data on the catalytic performance of the system under study and to further optimize it. As an alternative method of synthesis, the treatment of the starting amorphous silica in the medium of aqueous fluid at temperatures approaching the critical point of water or above it was chosen. It leads to the formation of crystalline phases without the use of alkali metal salts as chemical activators, which makes it possible to use the obtained samples as carriers that are definitely free of Na, W and Mn ions. The treatment was carried out in the media of water vapor and dense water fluid at temperatures below and above the critical point, respectively. The following main results were obtained:
- with an increase in the treatment temperature, the rate of transition of amorphous silica to quartz increases, and the formation of the target cristobalite phase can only be stabilized when processed in the subcritical region;
- the rate of the crystallization significantly decreases with increasing purity of the starting amorphous SiO$_2$, i.e. trace impurities (primarily sodium) present in the material accelerate the process;
- using the thermogravimetry method, the formation of hydrated forms of silica, containing bulk-bounded water – likely in the form of OH-groups – was detected; they drastically increase the mobility of structural elements, which leads to an increase in the rate of transition to thermodynamically more favorable crystalline forms at relatively low temperatures;
- when combining the treatment in water fluid and subsequent heat treatment, samples were synthesized that contain an almost pure cristobalite phase that does not contain impurities of ions capable of catalyzing oxidation processes;
- NaWMn/SiO$_2$-composites obtained by deposition of active components onto the synthesized samples of pure cristobalite practically do not differ in catalytic properties from systems of the same composition obtained by thermal synthesis; this can serve as a clear indication that catalysis proceeds exclusively with the participation of components present on the surface of the support.
The effect of a sharp (approximately 10-fold) increase in the activity of the NaWMn/SiO$_2$ catalyst without loss of selectivity in the oxidative coupling of methane to ethylene as a result of its treatment in a water fluid was observed. Kinetic analysis shows that this occurs as a result of an increase in the number of catalytically active species, but not at the expense of modifying their properties.

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Due to the high toxicity, carcinogenic and mutagenic activity of 1,1-dimethylhydrazine (unsymmetrical dimethylhydrazine, UDMH), the widespread use of this compound as a rocket fuel creates serious environmental problems. They are largely associated with the possibility of UDMH spills during its transportation, refueling of launch vehicles, cleaning of tanks with fuel residues, and emergency situations when launching rockets.

To eliminate the resulting polluted effluents containing rocket fuel, combustion with hydrocarbon fuel technologies are used, as well as oxidative reagent treatments (mainly for polluted soils cleanup). These technologies are far from perfect, having a high cost and lack of efficiency due to the variety of UDMH transformation pathways and the possibility of the formation of great number of toxic by-products. A modern alternative to existing technologies for the waste waters cleanup is the supercritical water oxidation (SCWO), which requires minimal energy and reagents and is most fully consistent with the principles of "green chemistry".

In the present study, the liquid and gas chromatography – high-resolution mass spectrometry was used to study the products of thermal degradation in supercritical water and SCWO of 1,1-dimethylhydrazine under the action of oxygen and hydrogen peroxide as oxidizers. It was established that with a lack of an oxidizing agent, as well as under the action of hydrogen peroxide, even under harsh conditions, a large number of hazardous products of the transformation of UDMH are formed, including carcinogenic \( N \)-nitrosodimethylamine. Experiments on varying the conditions of SCWO showed that the best results are achieved under the action of oxygen. It results in the formation of only trace amounts of nitrogen-containing products, among which
heterocyclic compounds predominate (mainly 1H-imidazole, 1-methyl-1H-1,2,4-triazole), and \textit{N,N}-dimethylformamide.

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OR-25

CYCLIZATION OF \( o\text{-NH}_2(C_6H_4)XH \) (\( X = \text{NH}, \text{O}, \text{S}, \text{CH}_2\text{NH} \)) IN SC CO\(_2\) CATALYSED BY THE TIN (II) DERIVATIVES

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Carbon dioxide in a supercritical state is attracted attention not only as a convenient reaction medium, but also as one of the most environmentally friendly and safe reagents, in particular, when interacting with various amines [1, 2]. Reactions of aliphatic diamines with CO\(_2\), leading to cyclic or linear derivatives of urea, proceed rather easily and are well known. Aromatic amines in these reactions require harsh conditions and the presence of a catalyst. At the same time, benzo-1,3-azol-2-ones, which are the products of cyclization of aromatic ortho-diamines, as well as their O- and S-containing analogues with carbon dioxide, are practically important heterocyclic compounds exhibiting a wide range of biological activity.

In the present work, we used tin (II) 2-ethylhexanoate and SnO as catalysts for the cyclization of model arylamines \( o\text{-NH}_2(C_6H_4)XH \) (\( X = \text{NH}, \text{O}, \text{S} \)) in SC CO\(_2\) with the formation of benzo-1,3-azole-2-ones. They possess about the same activity as the already known catalysts (TBA)\(_2\)(WO\(_4\)) [3] or [DBUH][OAc] [4], but they are advantageously low-cost and do not require a solvent. For comparison, we also carried out a cyclization reaction with a mixed diamine \( o\text{-NH}_2(C_6H_4)\text{CH}_2\text{NH}_2 \), containing both aryl and benzyl amino groups.

Reactions proceed with high (\( \geq 95\% \)) selectivity, the yields of benzo-1,3-azole-2-ones and 3,4-dihydroquinazolin-2-one under optimized conditions are presented in the
table below. The diamine $\text{o-NH}_2\text{(C}_6\text{H}_4\text{)CH}_2\text{NH}_2$, as expected, reacts an order of magnitude faster.

Table. The yields of the cyclization products under optimized conditions.

<table>
<thead>
<tr>
<th>X</th>
<th>$t$, h</th>
<th>$T$, °C</th>
<th>Catalyst</th>
<th>N eq.</th>
<th>Yield, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH</td>
<td>36</td>
<td>170</td>
<td>Sn(Oct)$_2$</td>
<td>0.40</td>
<td>90</td>
</tr>
<tr>
<td>O</td>
<td>36</td>
<td>210</td>
<td>SnO</td>
<td>0.40</td>
<td>27.5</td>
</tr>
<tr>
<td>S</td>
<td>36</td>
<td>170</td>
<td>SnO</td>
<td>0.40</td>
<td>64</td>
</tr>
<tr>
<td>CH$_2$NH</td>
<td>6</td>
<td>170</td>
<td>Sn(Oct)$_2$</td>
<td>0</td>
<td>100</td>
</tr>
</tbody>
</table>

Cyclization of 2-aminophenol with CO$_2$, catalyzed by SnO and resulting in benzoxazol-2-one, was carried out for the first time. At the same time, in the presence of Sn(Oct)$_2$, practically the only product in the reaction mixture is 2-(heptyl-3)-benzoxazole (the conversion of aminophenol in this case was 56%).

Possible reaction mechanisms depending on the starting arylamine and the catalyst used are proposed.

*This work was supported by RFBR (project no. 18-29-06010).*

**REFERENCES**

Homogeneous catalysis in liquid-phase reactions, as a rule, demonstrates higher efficiency and selectivity in comparison with heterogeneous one. However, transferring to gas-phase processes or chemical reactions in SCF, the application of homogeneous catalysts becomes impossible or quite difficult due to their insolubility (immiscibility) in such reaction media. Additionally, some limitations of homogeneous catalysts used for pilot-scale chemistry are well known. Therefore, the use of heterogeneous catalysts has no real alternative within actual chemical technologies, as well as for reasons of economic feasibility and benefit.

At the same time, widespread implication of heterogeneous catalysts in abovementioned reaction media like supercritical alcohols (sc-alcohols) give refuge for many difficulties and problems associated with a high reactivity of sc-alcohols with respect to some components of heterogeneous catalysts. The reducing properties of sc-isopropanol were previously described in detail by S.P. Gubin et al. for different salts and metal oxides, which are potential supports or active components of the catalysts. The revealed properties diminish significantly an area of application of such heterogeneous catalytic systems in tandem with sc-alcohols.

In the presentation, the authors will share their own experience of the use of heterogeneous catalysis in reactions carried out in sc-alcohols. In particular, the problem of different forms of silicas used in sc-methanol, features of metallic nickel catalysts application in processing heavy crude oil components, as well as the difference of behaviors of conventional hydrogenation catalysts (metallic nickel and palladium) in transfer hydrogenation with sc-alcohols will be touched upon.

The study was carried out by the financial support of the Russian Foundation for Basic Research in the framework of the research project No. 18-29-06022.
The modern tendencies in industry require the development of highly active and stable catalysts for different processes. Supported metal nanoparticles are one of the most prospective catalysts involved in the majority of the reactions (i.e. hydrogenation, oxidation, hydroformylation etc.), particularly in the size-sensitive processes [1]. Such nanocatalysts are characterized by unique properties (high surface area, high surface energy) and enhanced reactivity. However, the main problem of the metal nanoparticles is fast aggregation. In order to solve this problem, two main directions are used: (i) the search for highly effective stabilizers, and (ii) the development of novel synthesis methods.

Last years, the interest in the application of super- and subcritical fluids for the synthesis of the supported nanoparticles is raised. The formation of the metal particles in super- and subcritical fluids is classified as physical and chemical deposition [2]. This method is interesting from the point of view of the achievement of high dispersed nanoparticles with unique physical and chemical properties. It can concur with the classical wetness impregnation in terms of efficiency, rapidity, and safety. The use of water in the sub- or supercritical state in the catalyst synthesis (so-called hydrothermal synthesis) allows obtaining ultrafine metal oxides or metal nanoparticles from inorganic salts [3]. The metal precursor undergoes hydrolysis resulting in the formation of metal hydroxide, which then is converted into metal oxide or metal particles [4].

In this work, we report the physics-chemical study of the structure and catalytic performance of metal-containing catalysts synthesized in subcritical water. The
catalysts were prepared in the superheated water (T = 200 °C, P = 6.0 MPa) for 15 minutes with the following reduction in a hydrogen flow. Hypercrosslinked polystyrene (HPS) and silica were used as catalyst supports. Both the porous structure and the composition of the active phase were investigated in order to determine the processes taking place during the hydrothermal synthesis. The catalytic activity of the resulted supported materials was studied in a variety of the processes aimed at the production of liquid transportation fuel from the renewable sources.

This work was supported by the Russian Science Foundation (grant № 17-79-10089) and the Russian Foundation for Basic Research (grants № 17-08-00609, 19-08-00318 and 18-29-06004). Authors thank Dr. Alexey Bykov (Tver State Technical University) for XPS analysis of the catalysts and Dr. Liudmila Bronstein (Indiana University) for TEM study of the catalysts.

References

Today in the industry ethylene is produced mainly by thermal and catalytic cracking. These processes demand high temperatures (to 900°C), additional separation and purification of products. Another way to produce ethylene in the industry is the direct dehydrogenation of ethane. The direct dehydrogenation of light hydrocarbons to the corresponding olefins has several disadvantages. In catalytic dehydrogenation rapid carbonization and deactivation of the catalysts occurs. The oxidative dehydrogenation of light paraffins, in particular ethane, is the most effective method for producing olefins.

It was previously established that low-temperature oxidative dehydrogenation of ethane (ODE) with oxygen proceeds over MoVTeNbOx mixed oxide catalysts [1], which at a temperature (400°C) provide 90% ethylene selectivity at 60% ethane conversion. The effectiveness of MoVTeNbOx catalysts is associated with the presence of the orthorhombic M1 phase in their composition. The key problem when using this catalytic system is its low thermal stability and, as a result, irreversible deactivation.

For the first time [2] proposed the oxidative dehydrogenation of ethane under supercritical conditions. The activity of MoVTeNbOx catalysts in ODE was studied in a flow installation at pressures of 1–100 atm in the temperature range of 240–280°C. The N₂/O₂ = 2/1 mixture was obtained by continuous catalytic decomposition of N₂O on the hydroxylated catalyst HZSM-5 at the required pressure and temperature of 450 °C directly during the reaction in the reagent mixing unit.

It has been established that the use of supercritical conditions makes it possible to reduce the ODE temperature from 360°C at 1 atm to 280°C at 100 atm with an increase in ethylene productivity from 240 to 290 g(C₂H₄)·h⁻¹·kg⁻¹_cat, respectively. At
the same time, a high selectivity of ≈ 90% for ethylene is maintained. The catalyst is stable throughout the experiment (40 hours).

Table 1. The dependence of conversion (X), selectivity (S) of ODE on pressure over MoVTeNbO₉ catalyst.

<table>
<thead>
<tr>
<th>Pressure, atm</th>
<th>X (C₂H₆), %</th>
<th>X (O₂), %</th>
<th>Oxygen consumption, mol.%</th>
<th>S, %</th>
<th>Y, g(C₂H₄)/h⁻¹ kg⁻¹ cat</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>C₂H₄</td>
<td>CO₂</td>
<td>C₂H₄</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>1</td>
<td>100</td>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td>20</td>
<td>6</td>
<td>9</td>
<td>90</td>
<td>10</td>
<td>97</td>
</tr>
<tr>
<td>40</td>
<td>7</td>
<td>10</td>
<td>84</td>
<td>16</td>
<td>95</td>
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<td>60</td>
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<td>23</td>
<td>92</td>
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<td>90</td>
<td>13</td>
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<td>72</td>
<td>28</td>
<td>90</td>
</tr>
<tr>
<td>100</td>
<td>15</td>
<td>26</td>
<td>68</td>
<td>32</td>
<td>88</td>
</tr>
</tbody>
</table>

(T = 280 °C, P = 1 atm, v=1600 h⁻¹, C₂H₆:O₂=75:25; P=20–100 atm, C₂H₆:O₂:N₂=31:23:46, v=1000-2400 h⁻¹).

References:


Carbon dioxide is one of the important natural fluids (second least expensive solvent after water) and is widely used in various commercial and industrial applications. The remarkable anomalous thermodynamic and transport properties (see Figs. 1 to 3) of supercritical CO$_2$ and CO$_2$ containing binary mixtures are widely used in industry. During the past years, interest in using CO$_2$ has increased because of its advantageous thermodynamic and transport properties in supercritical conditions and its environmental impact (see Figs. 1 to 3). The purpose of the presentation is to assess the available information so as to obtain a general procedure for dealing with the critical enhancement of the thermodynamic and transport properties of supercritical CO$_2$ and CO$_2$ containing binary mixtures for practical and scientific applications. The present review provides comprehensive analysis of the thermodynamic and transport properties of supercritical carbon dioxide and CO$_2$ containing binary mixtures (experiment and theory) and their various technological and scientific applications in different natural and industrial processes. The available information for the thermodynamic and transport properties (experiment and theory) enhancement (anomaly) of supercritical carbon and SC CO$_2$ + solute mixtures is comprehensively reviewed. The effect of long-range order parameter fluctuations on the thermodynamic and transport properties of supercritical fluids (SC CO$_2$) will be discussed. Simplified scaling type equation based on mode -coupling theory of critical dynamics with two critical amplitudes and one cutoff wave number as fluid-specific parameters was used to accurately predict of the transport properties of
supercritical carbon dioxide. The recommended values of the specific parameters (asymptotic critical amplitudes) of the carbon dioxide for practical (prediction of the thermodynamic and transport properties of the supercritical CO$_2$ for technological applications) and scientific use were provided. The role of the critical line shapes of the carbon dioxide containing binary mixture (SC CO$_2$+solvent) in determination of the critical behavior of the mixture near the critical point of pure supercritical solvent (CO$_2$) is discussing. The Krichevskii parameter concept for a description of thermodynamic behavior of dilute near-critical SC CO$_2$+solute mixtures also is discussing. The structural and thermodynamic properties of the carbon dioxide containing binary mixtures near the critical point of pure solvent (CO$_2$) were calculated.

**Fig. 1.** Measured and calculated isochoric (left) and isobaric (right) heat capacities of CO$_2$ as a function of density and temperature in the supercritical region. Symbols are reported data; Solid lines are calculated from crossover model; Dashed lines are calculated from reference EOS (REFPROP,NIST).

**Fig. 2.** Measured and calculated thermal conductivities (left) and thermal diffusivities (right) of CO$_2$ along the supercritical isotherms and isobars as a function of density (left) and pressure (right). Symbols are reported data from NIST/TRC DATA BASE; Solid curves are calculated from reference correlation by (REFPROP, NIST).
Fig. 3. Critical curve data for series of binary CO\(_2\)+n-alkane mixtures in \(P_C - T_C\) projection.

This work was supported by Russian Foundation of Basic Research (RFBR) grants № 19-08-00056 and № 18-08-00500.
Currently, the issue of controlling the content of substances in systems operated under extreme conditions, for example, at elevated pressures and temperatures, is relevant. One of the methods for introducing an internal standard into the system for a relative assessment of the concentration of other substances is chromatodesorption systems, which is a matrix with an embedded indicator substance that is desorbed at normalized concentrations [1-2].

The purpose of this work was to develop a method for the production and testing of chromatodesorption systems (CDS) for use in liquids under extreme conditions. Polymers based on epoxy resins were chosen as the matrix for creating the CDS. Benzoic and stearic acids were used as an analyte. The obtained CDS were tested in a reactor under an elevated pressure of 5–20 MPa, at 50–230 ºC under static and dynamic conditions. Water was used as an extractant. The most optimal conditions for obtaining standard water solutions under various operating conditions have been established. Qualitative and quantitative control of the extraction of analytes was carried out by chromatography-mass spectrometry and high-performance liquid chromatography. Experimental desorption curves for water-soluble analytes from monolithic polymer composite material CDS were obtained.

We established that the analyte can be repeatedly extracted from the matrix in normalized amounts.

These systems can be used in extreme conditions (under elevated pressure and temperature), where required the constant monitoring, either for the direction of flow of the fluid, or to ensure an internal standard in the system for in-line monitoring of products.
References:


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EXPERIMENTAL STUDY OF THE CONDITIONS OF THE FORMATION OF TOPAZA SINGLE CRYSTALS, THEIR STRUCTURAL AND MORPHOLOGICAL FEATURES AND PROPERTIES

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Topaz is one of the most popular gems. Its monocrystals from chamber and rare metal pegmatites and hydrothermal veins are often characterized by a high degree of perfection and a variety of colors. However, topaz remains one of the few gems for which artificial growth methods have not yet been developed. In connection with the solution of this problem, we experimentally studied the stability and isothermal reactions of topaz and other minerals with aqueous solutions of KF and HF (concentrations from $10^{-4}$ to 10 m and from 0 to 1.0 m, respectively) at temperatures of 300–600 °C and pressure of 100 MPa. At the same time, the features of the transfer of silica and alumina under thermogradient conditions in fluoride, chloride and alkaline solutions at temperatures of 500-780 °C and pressures of 40-150 MPa were investigated in order to determine the possibility of growth of single crystals of topaz under such conditions.

It is established that for the stability of topaz in the indicated reactions, the solutions should have a high concentration of HF ($3 \times 10^{-3}$ - $8 \times 10^{-1}$ m) and a low concentration of KF ($< 7 \cdot 10^{-3}$ m). As the temperature rises from 300 to 600 °C, the stability field of topaz on the $\lg (\text{mHF}) - \lg (\text{mKF})$ diagram shrinks and shifts to higher HF concentrations. In the case of separate and / or joint dissolution of quartz, topaz and corundum, the transfer of silica and alumina under the conditions of a direct temperature gradient can be either single or multidirectional and depends on the temperature and pressure parameters and the composition of the solutions, which determine the sign of the temperature coefficient of solubility of these minerals.
Taking into account the obtained data, for the first time a reliable method was developed for growing single crystals of topaz on seed using autoclaves made of Cr-Ni alloy EI 437B at temperatures of 500-780 °C from low-density fluoride solutions. The crystals in daylight are either colorless or have a light green and blue color (Fig. 1, Fig. 2a). With electric lighting, the crystals change it to pink (Fig. 2b). Ultraviolet light causes bright red fluorescence in topaz crystals (Fig. 2c), caused by the presence of an admixture of chromium, which enters the solution during partial corrosion of the autoclave walls. The maximum growth rate of Cr-containing topaz (up to 0.2 mm / day) has the pinacoid face [001]. Initially, colorless crystals under the influence of ionizing gamma irradiation (dose 6 Megarad, $^{60}$Co source), like natural topaz, are colored in a reddish-brown color, which after annealing at 250 - 300 °C changes to blue.

Further improvement of the developed method can lead to the creation of an industrial technology for the production of synthetic topaz.

Fig. 1. External morphology of topaz single crystals grown in supercritical water-fluoride solutions.
Fig. 2. Coloring of synthetic Gr-containing topaz in daylight (a), electrical (b) and ultraviolet (c) illumination.
SOLUBILITY OF THE IODINE IN SUB- AND SUPERCRITICAL CARBON DIOXIDE

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Despite small volumes of receiving an iodine (world production about 10000 tons/year), it is of particular importance for the national economy [1]. For creation of effective technology of an iodine extraction with carbon dioxide as extragent it is necessary to possess data on solubility of an iodine in supercritical CO$_2$ and its dependence on extragent state parameters. In literature there are sketchy data on solubility of an iodine in supercritical fluids [2,3] while the solubility of an iodine in subcritical carbonic acid is almost not investigated.

The solubility of an iodine is determined by a dynamic method with use of the analytical extraction installation MV-10ASFE (Waters, the USA). The quantity of an iodine was defined iodometricaly, the quantity of CO$_2$ was calculated from operating conditions of the pump.

The general relative accuracy of determination of solubility of an iodine in carbon dioxide was 4.3%.

Before the measurement of solubility of an iodine in carbon dioxide feed rates of CO$_2$, degree of fullness of an extraction cell were determined.
Table. Solubility of an iodine in carbon dioxide, Y * 10^3

<table>
<thead>
<tr>
<th>Pressure, at</th>
<th>Temperature, °C</th>
<th>20</th>
<th>30</th>
<th>40</th>
<th>50</th>
<th>60</th>
<th>70</th>
<th>80</th>
</tr>
</thead>
<tbody>
<tr>
<td>60</td>
<td></td>
<td>0.122</td>
<td>0.130</td>
<td>0.140</td>
<td>0.155</td>
<td>0.202</td>
<td>0.214</td>
<td>0.238</td>
</tr>
<tr>
<td>80</td>
<td></td>
<td>0.125</td>
<td>0.160</td>
<td>0.165</td>
<td>0.192</td>
<td>0.220</td>
<td>0.242</td>
<td>0.251</td>
</tr>
<tr>
<td>100</td>
<td></td>
<td>0.126</td>
<td>0.168</td>
<td>0.210</td>
<td>0.252</td>
<td>0.294</td>
<td>0.336</td>
<td>0.378</td>
</tr>
<tr>
<td>150</td>
<td></td>
<td>0.127</td>
<td>0.169</td>
<td>0.229</td>
<td>0.316</td>
<td>0.404</td>
<td>0.491</td>
<td>0.578</td>
</tr>
<tr>
<td>200</td>
<td></td>
<td>0.128</td>
<td>0.172</td>
<td>0.230</td>
<td>0.353</td>
<td>0.474</td>
<td>0.597</td>
<td>0.719</td>
</tr>
<tr>
<td>250</td>
<td></td>
<td>0.128</td>
<td>0.180</td>
<td>0.237</td>
<td>0.423</td>
<td>0.609</td>
<td>0.796</td>
<td>0.981</td>
</tr>
<tr>
<td>300</td>
<td></td>
<td>0.146</td>
<td>0.220</td>
<td>0.360</td>
<td>0.567</td>
<td>0.776</td>
<td>0.983</td>
<td>1.191</td>
</tr>
<tr>
<td>350</td>
<td></td>
<td>0.214</td>
<td>0.415</td>
<td>0.616</td>
<td>0.817</td>
<td>1.019</td>
<td>1.220</td>
<td>1.420</td>
</tr>
</tbody>
</table>

Data presented at the table show that the solubility of an iodine increases if temperature and pressure increase. The mole fraction of an iodine (Y) in a saturated solution at 20 °C and 60 - 350 atm reached 1.2 - 2.14*10^-4 that corresponds to mass concentration of 0.035 - 0.062% that in 2,2 – 3,.9 times exceeds solubility of an iodine in water at this temperature [4]. Thus, the possibility of an iodine extraction from natural waters by liquid carbon dioxide is obvious. The solubility of an iodine at 350 atm and 70 - 80 °C reaches 0.35 - 0.40% that does possible cleaning an iodine paste from mineral impurity.

With increase of pressure the temperature gradient of solubility of an iodine considerably increases, and isobars are leveled. With a pressure of 350 atm an isobar of solubility of an iodine represents direct (R2 =1).

The results received in the real work well coordinate with the data which are available in literature for temperatures 40 and 50°C [3], a divergence in the compared experimental data does not go beyond an estimated total error of observed data. Good coincidence of the data with literary data obtained by authors for narrow temperature range serves as confirmation of correctness of the experiments put in work and reliability of results for temperatures from 20 to 80 °C.

This work was carried out using the equipment of CCU RO Arktika NArFU with assistance of the Russian Fundation for Basic Reseach (grant No. 18-44-292002 p_mk).
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In the critical region, the fluid is highly inhomogeneous, and its structure remains self-similar at all levels of spatial scale. Outside the critical region, the fluid is completely homogeneous, which provided the basis for simplifying and constructing equations of state, which allow calculating vapor-liquid equilibrium with high accuracy. The aim of the work is to create a well-defined hierarchical model that correctly describes the fluid in both areas. In the model under consideration, scale invariance arises naturally in the limiting case.

When approaching the critical point, the properties of the phases become similar. Surface tension decreases rapidly to zero. It becomes possible for liquid droplets to occur in the gas phase, and gas bubbles to occur in the liquid phase. When approaching the critical point, the diameters of the “liquid droplets” and “gas bubbles” grow. Gas bubbles and liquid droplets are not only spatially mixed, but also hierarchically placed into each other. Inside each drop there are gas bubbles, and inside each bubble there are liquid drops. Moreover, this situation is repeated at all levels of scale. Based on this picture, we reduce the entire complex structure of the fluid to consideration of only two phases, “droplets” and “bubbles”. Let's call this model the “two-phase hierarchical model” (TPHM). On this basis, we will explore how orderliness occurs at each scale level. For the initial approximation, we take the fluid, consisting of real molecules (zero scale). A system composed of a mixture of microbubbles and microdroplets will correspond to the first scale level. In the system of the second level of scale, “microbubbles” and “microdroplets” no longer consist of molecules directly - they are formed from “microbubbles” and “microdroplets” of the first scale level. The system of the n-th scale level is constructed in a similar way. The system of equations for TPHM is obtained from consideration of the hierarchically repeating Ising models. The coordination of fluid systems of different levels is performed by redefining the interaction energies of microdroplets and
microbubbles ("supercubes") of neighboring levels: the energies of $n + 1$ level are calculated from the known energies of the $n$ level.

For the self-consistent supercube system, the evolution of the heterogeneity structure of each level was calculated. A consecutive shift of the critical point towards a lower temperature is found when taking into account inhomogeneities of the $n+1$ scale level. For a number of pure substances, the value of the total shift of the critical temperature was calculated, and the agreement with the experimental data was shown. As expected, when approaching a critical point, the size of inhomogeneities quickly grows. At the same time, it was also found that the heterogeneities of all other scale levels remain. There is a difference in the behavior of inhomogeneities in cases of approaching the critical point from the side of low and from the side of high temperatures. Critical indices for the self-consistent system of "supercubes" are obtained. The BETA index is equal to 0.3212 (as is known the exact value is 0.326419). In MD simulation of a fluid with a Lennard-Jones potential [1], at pressures above the critical pressure and in a narrow density band, the presence of a "mesophase" was detected, the nature of which remains unclear. Our model gives an explanation of this phenomenon.

It is possible to generalize the theory to the case of mixtures consisting of molecules of different shapes and different types of intermolecular interaction. Choosing a lattice model of a fluid [2] (hole group-contribution model) as a zero approximation, using TPHM as a superstructure above it, binary and ternary mixtures composed of methane, ethane and propane were calculated. For these mixtures, phase diagrams and critical loci were calculated. The comparison of the obtained results with actual data demonstrates good agreement.

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THERMODYNAMIC AND TRANSPORT PROPERTIES OF SUPERCRITICAL FLUIDS: A REVIEW OF RESEARCHES OF RUSSIAN SCIENTISTS

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The review is devoted to the experimental study of the thermodynamic and transport properties of sub- and supercritical fluids, performed in Russia, and the assessment of its influence on the development of the modern theory of phase transitions and critical phenomena. Particular attention is paid to the pioneering experiments to study the critical behavior of the isochoric heat capacity and thermal conductivity, carried out by Russian scientists, which radically changed the classical understanding of the nature of critical and supercritical phenomena. The key role of the isochoric heat capacity in the study of critical phenomena and, in particular, the first experiments carried out in the vicinity of the critical point was discussed in detail. The classical and non-classical (scaling) theory of isochoric heat capacity, their role for fundamental scientific research in the field of critical and supercritical phenomena are analyzed. The questions of the relationship between the isochoric heat capacity (critical amplitudes and critical exponent) with fundamental variables and relations of the theory of critical phenomena are considered in detail. The special role of isochoric heat capacity in the development of the theory of "complete" scaling is emphasized. It is shown how new fundamental experiments on isochoric heat capacity changed our understanding of the contribution of saturated vapor pressure and chemical potential to the divergence of two-phase heat capacity at the critical point and contributed to identifying the nature of the asymmetry of the coexistence curve. The review will demonstrate the relationship of the fundamental knowledge of the thermodynamic and transport properties of fluids with the choice of ways to
improve the basics of supercritical fluid technologies. In particular, the boundaries of the region of state parameters in the $P – T$ and $\rho – T$ planes near the critical point will be established, where the influence of critical fluctuations on the behavior of the thermodynamic and transport properties is essential. This result is important for practical applications of supercritical fluids.

Pioneering studies of the thermal conductivity and isochoric heat capacity of water, carbon dioxide and ammonia near the critical point, as well as studies on heat transfer under conditions of natural convection of carbon dioxide and sulfur hexafluoride with subcritical and supercritical parameters of the substance are considered. Analysis of the current state of research on heat transfer under conditions of forced convection of a supercritical coolant has been presented elsewhere [1]. A variety of factors affecting the purity of the experiment in the vicinity of the critical point resulted in a long-standing discussion about the presence / absence of a peak of thermal conductivity coefficient in the near supercritical region. Its result was the adoption of a correction of the Standard Tables for transport properties of water and carbon dioxide. Due to the correction, the values of the Prandtl number in the critical region were significantly (up to two or more times) reduced. In experiments with ammonia, attention is drawn to the fact that the nonmonotonicity of the course of the thermal conductivity curve in the vicinity of the critical isochore can be traced very far from the critical point, at a distance of one hundred degrees. Clarification of specific mechanisms that transmit the influence of the critical point at a significant distance from it is referred by D.Yu. Ivanov [2] to the key issues that determine the understanding of the nature of critical phenomena. In contrast to the results of thermal conductivity of supercritical fluids, the peak of the heat transfer coefficient on supercritical isotherms was revealed by almost all researchers. Its existence is traditionally associated with the phenomena of increasing heat capacity and convective mobility of the near-critical medium.

The discussion of the pulse measurements data in the final part of the review showed that literally the first change in the experimental conditions (traditionally stationary) led to a change in the essence of the results [3]. Obviously, the award of the Nobel Prize to Kenneth Wilson and the adoption of new Standard Tables for transport
properties have not completed the study of thermal physics of critical phenomena: the object under study turned out to be more complicated than initially thought.


Today, the topical issue in the production of rare-metal products is the development of highly efficient technologies for the extraction of rare-earth metals (REM) from both rich and poor, difficult to open raw materials [1]. One of the promising secondary sources containing rare-earth metals in Kazakhstan is phosphogypsum, a waste resulting from the processing of Karatau phosphate rock. The total content of rare-earth metals in this raw material reaches ~ 0.5% mass. Currently, the volumes of phosphogypsum dumps of the company TF “Kazphosphate” LLP “Mineral Fertilizers” amount to over 13 million tons, and there is an annual increase in the volume of dumps by 1 million tons [2]. When phosphogypsum is stored in open areas, environmental pollution occurs. It dusts in the air, leaving harmful impurities, and these impurities also pollute aquifers and water bodies, as some of them are water soluble. Therefore, the issue of phosphogypsum processing is acute in all countries with such waste.

The aim of the research is to develop highly efficient, energy-saving supercritical technologies for processing raw materials and industrial wastes for the extraction of rare-earth metals.

In this paper, we studied the processes of extracting yttrium, cerium, and lanthanum from phosphogypsum under ordinary and supercritical conditions. Modes of effective transfer of rare-earth metals into a solution from phosphogypsum (composition of decomposing mixture, S: L ratio, leaching time, microwave frequency, pressure and temperature) in open and autoclave mode with microwave preparation (“Speedwave4”, Berghof) are established. The use of the HNO₃-H₂O₂ mixture in open conditions allows achieving the following extraction rates: Y – 116.4 ppm, Ce – 143 ppm, La – 89.4 ppm. In the mode with microwave preparation, the highest
extraction rates are achieved with the use of \( \text{H}_2\text{SO}_4 \) decomposition. \( \text{H}_2\text{O}_2 \): Y – 179 ppm, Ce – 148.8 ppm, La – 134.6 ppm. A quantitative analysis of rare-earth metals was performed by the ICP-MS.

Extraction of yttrium, cerium and lanthanum was carried out from standard nitric acid solutions, and from leaching solutions of phosphogypsum. As extractants, solutions of tri-n-butyl phosphate (TBP) and di-2-ethylhexyl phosphoric acid (D2EHPA) in kerosene were used. The optimal conditions for the extraction of rare-earth metals from their standard solutions were determined, for yttrium: \( T = 3 \) min., \( C_{\text{D2EHPA}} = 10\% \), O: B = 1: 10. The experimental data obtained were used for supercritical \( \text{CO}_2 \) extraction of rare-earth metals. From the literature [3-4], it was found that the extraction of lanthanides in supercritical carbon dioxide saturated with TBP-HNO\(_3\) adduct from their oxides proceeds more efficiently with increasing pressure from 85 to 250 atm. and lowering the temperature from 80 to 33 °C. A standard metal solution was placed in a cell for extraction, the extractant, TBP or D2EHPA, was added in a ratio A: B = 1: 10. The concentration of TBP in SC-CO\(_2\) was 3% by weight, the temperature in the system was 45 °C, the pressure was 200 bar. Extraction in the Y-D2EPHA-SC-CO\(_2\) system was carried out according to the above method. The results indicate the promising use of the supercritical \( \text{CO}_2 \)-extraction method for extracting rare-earth metals from phosphogypsum leaching solutions.

**BIBLIOGRAPHY**


HIGHLY POROUS LUMINESCENT MATERIALS BASED ON POLYMERIC MATRIXES IMPREGNATED WITH MOLECULES OF THE CHELATE COMPOUNDS IN THE SCF MEDIUM

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The possibility of luminescent films making based on new highly porous polymer matrices doped with a chelate complex of the Eu (dbm)\(_3\)·H\(_2\)O type in a supercritical fluid (SCF) medium was demonstrated. As such, supercritical carbon dioxide (scCO\(_2\)) was used with a small addition (5vol.%) of ethanol as a co-solvent. Source materials for these purposes were selected polytetrafluoroethylene (PTFE) films, obtained by the special technology of thermal precipitation (stretching of films in a heated state) or electrospinning (synthesis from a melt in an electric field). In addition, polybenzimidazole (OPBI) films [1] with foam-like oriented structures, which were formed on their surface using laser radiation at 405 nm, were also used. The possibility of creating luminescent films based on new highly porous polymer matrices doped with a chelate complex of the Eu (dbm)\(_3\)·H\(_2\)O type in SCF was demonstrated. Source materials for these purposes were selected samples of films of polytetrafluoroethylene (PTFE), obtained by the technology of thermal precipitation (stretching of films in a heated state) or electrospinning (synthesis from a melt in an electric field). Precipitation of the europium complex in the pores of these matrices (up to several microns in size) during impregnation leads to the appearance of photoluminescence (PL) in the red region belonging to the Eu\(^{3+}\) ions [2]. To verify
the efficiency of the SCF impregnation method, experiments on impregnating these matrices in a solution of ethanol with chelate molecules and washing of the SCF impregnated samples in pure ethanol were performed. Study of the PL spectra in all samples showed that in this case the efficient way of polymer matrices impregnation with chelate complex using sc CO\textsubscript{2} (compared to the saturation in ethanol solution) was realised. At the same time, the most intense PL is observed in PTFE samples obtained by electrospinning. An analysis of the intensity ratio of the electric dipole and magnetic dipole components of the PL spectra also makes it possible to suggest about changes in the nearest environment of the Eu\textsuperscript{3+} ions in each of the matrixes in all the considered cases related to impregnation and their further processing. As it turned out, for luminescent films obtained using SCF impregnation, the nearest environment of the rare-earth ion is realized as close as possible to the environment in the initial crystalline Eu (dbm)\textsubscript{3}·H\textsubscript{2}O compound.

Thus, the developed technologies for the synthesis of matrixes on the basis of PTFE keep the formation of a large number of associated pores with a wide dispersion in size, which makes it possible to simply modify their properties by impregnation with various precursors. At the same time, easy access of gas molecules to the internal volume of the sample is maintained. This is a particularly important point for various sensory applications of such materials, for example, as a chemosensor for the admixture of ammonia in the surrounding atmosphere [3]. In the case of a porous material based on an OPBI matrix with laser-induced foam-like structures, the technology developed for their preparation and their functionalization with various kinds of chelate molecules gives the possibilities for their application not only in sensorics, but also in the field of polymer optoelectronics, in creating protective markings for various products etc. The proposed new laser-induced method for the synthesis of local highly porous structures showed a high efficiency of introducing into them (almost an order of magnitude higher than in the main matrix) similar impurities using the SCF impregnation method.

This work was supported by Russian Foundation for Basic Research, grants No. 18-29-06056 and No. 18-33-00645 mol_a.


Supercritical fluid technologies, finally established in their status in the 70s of the last century, formed new boundaries of professional interest in such a concept as solubility. If in previous years this concept was primarily associated with the equilibrium concentration of the solute, as a rule, in a liquid organic solvent, then in the updated realities of extremely important and promising SCF extractants and solvents (dense gas state) with an anomalous increase in compressibility and other properties asymptotic proximity to the critical point against the background of practically incompressible solvents in the liquid state, a significant scientific space has been formed for studying, refining and expanding the classical their views. This, above all, is about such issues to be carefully considered, such as: the limits of applicability of the concept of solubility in SCF media and the linking of this concept with the variety of types of phase equilibria; crossover behavior of isotherms of solubility of substances in SCF solvents; the comparative efficiency of extraction processes based on selective dissolution for cases of liquid-phase and supercritical fluid extractants and, again, the linking of this issue with the type of phase equilibrium for the “solute-solvent” system; search for predictive possibilities within the framework of the issue under discussion and, finally, the study of the merits of a different physical and chemical nature (outside of CO₂ and H₂O) of solvents used in the SCF condition.

Regarding the limits of applicability of the concept of solubility in SCF media and linking this concept with a variety of types of phase equilibria, it suffices to dwell on
one simple example: in the best from the point of view of substance coverage, analysis of the quality of experimental data and the amount of material, reference book on the solubility of substances in SC-CO$_2$ [1] under the above-mentioned status, a sufficiently large amount of experimental data was obtained, obtained on the basis of the composition information for the steam branch of the binary system of the CO$_2$ system (I and II types of phase behavior according to D.F. Williams). It would seem easy to understand that only the top of the binodal obtained for a certain temperature, characterizes the critical pressure, and everything that precedes this and assumes the existence of a phase boundary is subcritical and has no relation to SC-CO$_2$. Erroneous perception is due to the fact that for such systems with supercritical parameters in this case of carbon dioxide there is no phase separation between the dissolved and solvent and the content of the first in the second is determined not by the main thermodynamic parameters of the dissolution process, but by the amount of dissolved. As a result, in the absence of visualization of the phase state of the object under study, they often erroneously operate with the concept of the filling level of the measuring cell through which SC-CO$_2$ circulates, assuming that insufficient filling does not provide sufficient phase contact time and leads to underestimated non-equilibrium results, while excessive filling of the same experimental cell contributes to drip entrainment and obtaining obviously overestimated results. Thus, in the case of binary systems related to phase behavior of types I and II, the liquid – vapor phase equilibrium characteristics are actually represented only by binodal, which eventually form a kind of continuous critical curve, and the concept of solubility in SCF solvent is simply absent. In the case of a different phase behavior of the thermodynamic system with a discontinuous critical curve (for example, IV and V types) with parameters corresponding to the SCF solvent state, there is a clear phase boundary, which rather easily allows the correct implementation of static and dynamic solubility studies. This state of affairs fully explains and confirms the previously established preference for using SCF extraction process (as opposed to liquid) [2] in cases where the “soluble – extractant” is a system with a continuous critical curve. Finally, it should be noted that the nature of the solvent can significantly influence and determine the type of phase equilibrium with one or another solvent.
The research has been carried out with the financial support of Russian Science Foundation (project No. 18-19-00478).


Development of new industrial processes is one of the most important modern tasks of researchers in the field of chemistry and chemical engineering. The existing environmental, economic and technological problems put chemical engineers in a position to create new "green" sustainable approaches to different reactions. One of the ways to solve such problems is the use of supercritical fluids as effective solvents and reagents for chemical processes [1, 2]. However, the use of the supercritical approach is one of the key in the development of "green chemistry". However, the selection of an effective catalyst, which will maintain its activity and selectivity in the processes carried out in supercritical conditions, also contributes to the solution of existing problems.

Most catalytic reactions are multi-phase. The main problem of such processes is external and internal diffusion limitations, which lead to the complexity of their scaling, as well as the need to use harsh conditions [3]. These problems can be solved by using a solvent. However, the "ideal" solvent must have special physical and chemical properties. A supercritical fluid with unique physical and chemical properties can be such an "ideal" solvent [4, 5]. In addition, numerous studies show that supercritical fluids provide improved selectivity for the target products, reduce the temperature of many processes and facilitate the separation of the final mixture.

The most frequently used supercritical fluids in chemical processes – water and carbon dioxide – are also environmentally safe [6-8].

This paper presents the results of the use of supercritical fluids (water, carbon dioxide, hexane) in catalytic reactions of organic synthesis, including: nitrobenzene...
hydrogenation, furfural hydrogenation, naphthalene oxidation, deoxygenation of carboxylic acids and their derivatives, hydrolytic hydrogenation of cellulose. Polymer-stabilized noble metals (Ru, Pd, Au) based on super-crosslinked polystyrene were used as catalysts.

Studies have shown that the use of supercritical fluids significantly affects the technological parameters of the studied processes in comparison with traditional solvents. It was noted an increase in selectivity to the corresponding target product in comparison with the processes carried out in the medium of classical solvents.

The work was supported by the Russian Foundation for Basic Research (grants №18-08-00404, 19-08-00318 and 18-29-06004) and the program UMNIK (agreement 50098).

References

Bacterial cellulose (BC) is a polysaccharide produced by a limited number of bacteria. BC has biocompatibility and slow biodegradability, microporous structure and good mechanical properties. Due to these properties, BC has various applications in biomedicine: artificial skin and artificial blood vessels, wound dressings and many others [1]. However, the lack of certain properties in BC (for example, antimicrobial activity that is very important for use in medicine) limits its use. In this connection, various BC-based composites, which improve its properties in comparison with pure BC, are of great interest [2]. Among the polymers used for composite synthesis, chitosan, gelatin and collagen have been successfully combined with BC to improve its biological properties [2]. Since it is well known that the widespread biopolymer chitosan has such properties as biocompatibility, non-toxicity, pronounced antimicrobial properties, it is widely used in various biomedical applications [3]. In this regard, composites based on BC and chitosan can be very promising material for applications in biomedicine. The presence of functional N-H and O-H groups provide strong hydrogen bonds between the molecules of the BC and chitosan. In a number of studies, it has been shown that BC/chitosan composites demonstrate pronounced improvements in mechanical and biomedical properties [4].

However, biomedical applications require high purity, including the absence of any solvent residues. As an substitution to acetic acid, a solution of carbonic acid can be used to dissolve chitosan, namely water saturated with carbon dioxide at a pressure of several hundred of bars. This is a unique medium, because, firstly, it is absolutely
biocompatible and self-neutralizing, since it decomposes spontaneously into pure water and carbon dioxide during decompression; and secondly, by varying parameters such as pressure and temperature, it is possible to control the pH of the medium, and, therefore, its ability to dissolve chitosan without adding any additional chemical agents. Thus, the purpose of our research was the development of methods for obtaining BC/chitosan-based composite materials from carbonic acid solutions. In the figure below you can see the scheme of the experiment on the synthesis of the BC/chitosan composite. The chitosan powder is placed in the high-pressure reactor (mini-autoclave-cuvette), after which water is added, and then CO₂ pressure is raised up to 300 bars. After the dissolution of chitosan, a film of bacterial cellulose is added to the solution, and then pressure is again raised up. Quantitative determination of the deposited chitosan is determined by the tritium label method.

According to the results of FTIR spectroscopy of the obtained composite films, we showed that there are amino groups in the composite, which indicates the presence of chitosan in the film. It was also shown chitosan macromolecules, penetrating into the cellulose matrix, break hydrogen bonds between hydroxy-groups of the BC, which reduces the crystallinity of the BC, and that further affects the mechanical properties (however, the effect is insignificant). In addition, the obtained samples were examined for mechanical properties, and their structure was studied by the SEM method.
References


Acknowledges

The reported study was supported by RFBR, research project № 18-29-06049 мк.
The creation of biological xenografts intended for the replacement therapy of soft tissue injuries is an urgent task of modern tissue engineering. However, effective engraftment and gradual replacement of the graft with newly formed recipient tissues depend on a number of properties, including biocompatibility, similar to native biomechanical characteristics, biodegradation rate, combined with the formation of a new recipient tissue, etc. Personalization of the listed properties is necessary for effective integration of xenograft into recipient tissue. In our work for this purpose, we used a combination of methods for decellularization, structuring with cross-linking agents, and extraction in supercritical fluid carbon dioxide (SCF-CO$_2$). The bovine pericardium, widely used for surgical reconstruction of soft tissues was used as a model system.

Decellularization is aimed at eliminating antigens from tissue of xenogenic origin, crosslinking agents increase resistance to biodegradation, and SCF -CO$_2$ alters the biomechanical properties of polymeric materials. The extraction technology in SCF-CO$_2$ is distinguished by its economic availability, environmental safety and programmability. The work included 3 stages:

- Getting a line of decellularized bovine pericardium, structured by various crosslinking agents: diisocyanate, epoxy compound, carbodiimide and genipin;
- Selection of treatment modes in the SCF-CO$_2$ environment by a combination of key parameters: temperature, pressure, flow rate;
Study of biomechanical properties, cytotoxicity, microstructural organization and proteolytic resistance of tissues before and after treatment with SCF-CO₂.

Based on the data obtained, it was concluded that all samples show a tendency to decrease the Young’s Modulus after treatment in the SCF-CO₂ environment (37°C, 15 MPa), which was observed both in experiments on uniaxial tension and during nanoindentation. Moreover, SCF-CO₂ did not affect the levels of cytotoxicity and proteolytic stability acquired as a result of crosslinking agents structuring. Thus, it was shown that with the help of supercritical fluid extraction, it is possible to control the mechanical properties of structured decellularized pericardiums, which is of interest for prosthetics of soft tissues with low Young Modulus values, such as blood vessels.


This work was supported by the Russian Foundation for Basic Research (Grant No. 18-33-00982).
Products made of polylactic acid or of its copolymers with glycolic and caproic acid and which degrade in organism producing non-toxic substance may be used for temporary prosthetics of bones and conjunctive tissue. Polymers may contain various additional active pharmaceutical ingredients such as resolvents, anticancer drugs, vitamins etc. The promising method for doped materials obtaining is impregnation of polymers in supercritical solvent, \( \text{scCO}_2 \).

An important characteristic of the materials containing biologically active substances is kinetics of dopant release to outer media during polymer swelling and hydrolysis. Development of reliable model of dopant release process will allow constructing systems “polymer – dopant” with required kinetic properties. Due to the fact that degradation of polyesters in water is quite complex process that includes steps of polymer swelling, pores formation and autocatalytic hydrolysis, reliable mathematical model of the dopant release still doesn’t exist.

In the report results of kinetic research of TEMPOL, AT and R3 (fig. 1) release from D,L-polylactic acid films will be presented. All the substances are stable nitroxide radicals, which enables using EPR spectroscopy for the investigation of process of their release to outer media and also the processes of polymer swelling and degradation.

Radicals were introduced in polymeric matrix by impregnation of polylactic acid in \( \text{scCO}_2 \) (310K, 160 bar). Obtained after CO\(_2\) pressure relief foamed material was milled and pressed into films 200 \( \mu \)m and 50 \( \mu \)m thick at 60\( ^\circ \)C. Fragments of the films containing various spin probes were immersed in phosphate buffered saline (PBS, pH 7.4), which imitates internal environment of the organism, and were kept at 37\( ^\circ \)C. The rate of dopant release from polymeric material was calculated from
amount of paramagnetic substance in samples of solution. Information concerning processes of swelling and degradation of polylactic films was obtained by shape analysis of EPR spectra of radicals inside the material. Magnetoresonance parameters of the radicals AT and R3 depend on the value of local pH, which allowed extracting additional information about degradation processes of polymeric samples. In particular significant decrease of pH (from neutral to < 5) inside films within first 10 days of keeping in PBS was established. The decrease is caused by autocatalytic process of polylactic chains hydrolysis.

![Fig. 1. Structures of paramagnetic dopants.](image)

TEMPOL

AT

R3
CREATION OF BIODEGRADABLE POLYMERIC STRUCTURES BASED ON D, L-POLYLACTIDE DOPED WITH BIOLOGICALLY ACTIVE SUBSTANCES

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The work is devoted to the creation of polymeric films and porous structures based on D, L-polylactide doped with biologically active compounds. Impregnation of the polymer occurs at the stage of the formation of a porous matrix using supercritical fluid carbon dioxide. The resulting matrices have a uniform porosity, permeable pores and a uniform distribution of dopant molecules in the sample. To obtain films with a thickness of 200 μm, the porous polymer containing the biologically active dopant is crushed, and the resulting powder is pressed at a temperature of 60°C. Nitroxyl spin probes TEMPONE, TEMPOL and spin-labeled nonsteroidal anti-inflammatory drug compound diclofenac (Fig.1) are used as biologically active substances, which allows to study the obtained samples using electron paramagnetic resonance spectroscopy.

Fig.1. Spin-labeled diclofenac

In the report the release kinetics of dopants of various structures from films and porous matrices into phosphate buffer solution will be presented. Also the stability of
the nitroxyl paramagnetic fragment inside the polymer matrix placed in bovine embryo serum and ascorbic acid solution will be analyzed.

This work was supported by the Russian Foundation for Basic Research (grants 17-02-00445 and 18-29-06059).
ORY-5

FUNCTIONAL PROPERTIES OF PHOTOPERPRISED METAKRIL DERIVATIVES OF POLYLACTIDE OBTAINED IN SC-CO₂

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With the development of regenerative and tissue engineering polylactide (PLA), environmentally friendly biodegradable polymers have become actively used to create bioresorbable implants, pins, surgical thread and sutures material. This was possible due to the high biocompatibility of these polymers as well as the ability to hydrolytically cleave and eliminate from the body with metabolic products. However, some properties of PLA, such as high fragility, hydrophobicity and insufficient adhesion to cells, do not allow to fully using of its potential. Therefore, giving polylactide the required physical and mechanical characteristics is an important problem. One of the potential ways of varying the properties of PLA is the introduction of additional modifying photoactive fragments through its terminal functional hydroxyl and corboxyl groups. This is done in order to obtain three-dimensional structures from it using laser stereolithography methods. However, the insufficient of reactivity of these groups limits the possibilities of chemical modification of PLA.

In the present work, in the environment of supercritical carbon dioxide, we was introduced methacrylate groups into the poly (D, L-lactide) molecule (Mw=5000 Da) through the urethane formation reaction. Conducting the modification reaction in a sc-CO₂ environment in two stages and with an excess of modifying agents allowed us to obtain the target product with a yield of more than 80%. After removal of the supercritical fluid, the methacrylated PLA was a dry crystalline mass, solvent free and ready for further use. The study of the features of the photopolymerization of a
modified PLA with the participation of a photoinitiator (Michler's ketone) showed a high reactivity of unsaturated bonds of the introduced methacrylate groups. We also found that oligourethanemethacrylate (OUM), which is formed as a by-product in the reaction of urethane formation, plays the role of a crosslinking agent in the process of photopolymerization of PLA. It was found that the optimal content of OUM for obtaining stable crosslinked structures is about 15%. Based on these data, a photoactive composition was prepared, from which three-dimensional cross-linked structures (scaffolds) were obtained using laser stereolithography, namely two-photon laser printing (Fig. 1). The non-toxicity of such systems has been established, which makes it possible to use them as a framework of cells in regenerative methods of tissue engineering.

![Fig. 1. Three-dimensional cross-linked structure (scaffold), obtained as a result of two-photon laser polymerization of a composition consisting of a modified methacrylate-containing PLA, OUM and photoinitiator.](image)

*This work was supported by the RFBR grant No. 18-33-00968 mol_a.*
The process of aerogels based on biopolymers obtainment consists of the following stages: gelation, solvent exchange, and supercritical drying. The solvent exchange and supercritical drying stages takes considerable time. Carrying out the solvent exchange stage under pressure in the carbon dioxide allows to intensify its. In addition, this method allows you to combine this process and supercritical drying process in one apparatus.

Theoretical and experimental studies of supercritical processes was carried out on the example of the process of aerogels obtainment with the aim of combining the two most important stages, solvent exchange and supercritical drying in one apparatus and its intensification. Properties of the systems were theoretically studied when the parameters were changed, namely the phase equilibrium in the three-component system “carbon dioxide - water - organic solvent”. An algorithm is proposed for calculating phase equilibrium in multicomponent systems under pressure. The experimental facility for carrying out supercritical processes has been modernized, which allows experimental investigation of phase equilibrium in multicomponent systems and the carrying out of the stage of solvent exchange under pressure. Experimentally investigated the process of solvent exchange under pressure for various parameters. On the basis of the data obtained, the most suitable conditions for the solvent exchange process were selected and step-by-step solvent exchange was experimentally implemented. It has been shown that the implementation of the solvent exchange under pressure reduces the required process time compared to traditional solvent exchange without using carbon dioxide by 5.5 times. The results of the work allow developing a highly efficient technology for producing aerogels based on biopolymers.

The reported study was funded by RFBR according to the research project № 18-38-00420.
Aerogels are the lightest of the known solid materials and have a huge potential for use in various applications. Aerogels consisting of two or more different materials are the most promising [1], for example, aerogels with embedded carbon nanotubes (CNTs). The use of various raw materials allows maintaining the unique properties of aerogels such as: low density, high porosity and specific surface area, and at the same time giving the material new functional properties: strength, electrical conductivity, hydrophobicity, sorption selectivity.

During production of hybrid aerogels with nanotubes, CNTs tend to form aggregates due to the action of van der Waals forces. The formation of aggregates affects hybrid aerogels’ structure and, as a result, their characteristics. Control of the aggregation process allows producing materials with required properties. The distribution of nanotubes in a material is influenced by various factors: surface’s chemical composition, dimensions, synthesis method, concentration of nanotubes [2]. In addition, the type of polymer matrix and its physicochemical properties also affect the uniformity of distribution. As it is known from the literature survey, the following approaches and their combinations are used to obtain a uniform nanotubes distribution: mechanical methods (calendering, use of ball mills, homogenization, ultrasonic treatment) and use of surface-active substances (surfactants). Functionalization of CNT surface can also improve distribution.

This work is devoted to the methods for producing silica aerogels and alginate aerogels with embedded CNTs using the supercritical drying process, mechanisms of structure formation were studied. In addition, sorption properties of aerogels with CNTs were investigated.
The fundamental objective of the work is the development of materials for the petrochemical complex capable of sorbing methane. In the future, new materials will be able to store natural gas as a motor fuel without ultra-low temperatures, high pressures and heavy metal vessels. The most promising for solving this problem are carbon nanomaterials, in particular, carbon aerogels, i.e. 3D porous structures consisting of nanoscale particles. They are obtained by pyrolysis of organic polymer precursors. Resorcinol formaldehyde aerogels, which are easily synthesized by resorcinol and formaldehyde polycondensation followed by supercritical drying, are usually used as a precursor.

Published data indicate that carbon aerogels mainly consist of amorphous carbon, in which graphene-like structures begin to appear. In addition, several examples of graphene-based aerogels are described in the literature. The purpose of this work is to estimate the interaction energy between methane and graphene, as well as graphene-like materials to determine the prospects for using carbon aerogels as methane accumulators.

It is known that the interaction of methane with a graphene layer is van der Waals, and to study the adsorption properties of graphene aerogels of arbitrary structure, it is sufficient to know the interaction potentials of the methane molecule with one graphene layer.

To solve this problem, we present a quantum-chemical model of various graphene structures containing adsorbed methane. An example of the initial system is shown in Fig. 1. To calculate the interaction energy, the PRIRODA software package and the effective Hamiltonian well describing dispersion interaction were used. The obtained
interaction potentials are shown in Graph 1 (values of distances in Å and interaction energies in kcal/mol are shown).

From the data obtained it is clear that with a suitable distance between two graphene planes, the total interaction energy of methane can reach 3.5 kcal/mol, which is several times higher than the heat of evaporation of methane.

The phenomenon of changes in critical points and boiling points for methane under the conditions of interaction with the graphene plane was also investigated. According to preliminary data, the boiling point of methane rises by more than 100°C.

Figure 1. Methane molecule on the graphene layer

Graph 1. The interaction potentials of CH₄ with the model of a graphene layer at different mutual orientations
We developed a new approach to establish the structural modifications of supercritical fluids (SCF). Comparative measurements of two optical parameters — molar refraction and nonlinear refractive index are used as an indicator of the state of the medium. Significant changes in these two parameters are caused by the modification of the medium optical properties in the SCF region where the clustering of the medium is occured (critical point, Widom line). Thus, using relatively simple (compared with, for example, X-ray or neutron analysis methods) optical techniques; it is possible to obtain not only qualitative but also quantitative information on the clustering of SCF. We developed a computer simulation technique based on an analytical model and molecular dynamics. Experiments were performed using a femtosecond Cr:Forsterite laser impulses that confirm the validity of this approach, namely, the presence of a sharp increase in the nonlinear refractive index in the vicinity of the Widom line. The growth of the nonlinear refractive index is confirmed by the change in the efficiency of nonlinear-optical processes occurring during the interaction of high-power femtosecond laser pulses with supercritical fluid. It is shown that the supercontinuum generated in the monofilamentation regime (self-channeling of a high-power femtosecond laser pulse) (spectrally superimposed laser pulse) has the widest spectrum in the vicinity of the Widom line.
We discussed a new approach of changing the regime of clustering in supercritical media through the use of a binary mixture (for example, Xe-CO$_2$, Xe-SF6), which, accordingly, should lead to a change in nonlinearity. The developed diagnostics of SCF modification in the area of its clustering remains applicable. Such mixtures, representing a medium with synthesized nonlinearity, can be used to increase the generation efficiency of supercontinuum (as a new coherent wideband source for spectroscopic measurements) due to a combination of a high nonlinear refractive index of atomic Xe combined with the presence of the molecular part of the nonlinear refractive index of the second component. As a result, in such a mixture, the generation of a supercontinuum will occur more efficiently than in each medium separately.
Here we demonstrate a one-step method for preparation of complex silver-gold nanoparticles (NPs) of core-shell type in a supercritical CO$_2$ (scCO$_2$) media, and an experimental setup for its realization. The created system allows to control the process of accumulation and sedimentation of NPs in a high-pressure reactor in real time according to the optical absorption spectrum both during the ablation process and for a certain period of time after the laser is turned off. The time dependences of the absorption spectra of formed NPs are analyzed for various laser irradiation regimes and fluid parameters in the reactor. The comparison of the obtained results with objective electron microscopy data is given. The advantages of using scCO$_2$ for the formation of such NPs are discussed. The possibilities of the used approach for the controlled synthesis of composite NPs with specified characteristics and their application are also analyzed.
Aerogels are a class of highly porous materials that have a high specific surface area and low density. These properties allow the application of aerogels in various fields of science and industry, in particular, as heat insulating materials and carriers of active substances in the pharmaceutical industry. The objective of creating aerogels with specified properties is always associated with the need to carry out a large number of experiments. The development of models that allow generating aerogel structures adequate to experimental samples and predicting their properties will reduce the amount of experimental research and reduce the cost of creating new aerogels.

In this work, models that allow to generate structures of various aerogels and to predict their properties with high accuracy - thermal conductivity and mechanical properties (Young's modulus) were developed. To generate model structures of aerogels, a cellular automaton model based on the diffusion-limited cluster aggregation method was developed. This model takes into account the presence of secondary clusters in the structure of aerogels. This allows to take into account the influence of the conditions of the process of obtaining aerogels and create model structures that correspond with high precision to experimental samples.

The developed models for predicting thermal conductivity and Young's allows taking into account the heterogeneous structure of an aerogel, which consists of a solid backbone and air-filled pores.

Computational experiments on the generation of structures of silica-resorcinol-formaldehyde and polyamide aerogels were carried out. Model structures of the aerogels were created and compared with experimental samples. For the created model samples, computational experiments were carried out to predict their properties — thermal conductivity and compressive strength.
ENERGY EFFICIENCY OF WATER + 1-PROPANOL SUPERCritical FLUID AS A WORKING SUBSTANCE OF STEAM POWER PLANT

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Water is a main working substance in thermodynamic cycles of steam power plant (SPP), particularly, of thermal stations which diapason of working temperatures is near critical and supercritical regions. Efficiency of SPP depends on changes of properties of working substances in working cycles at different p and T [1]. To enlarge the diapason of working temperatures of heat energy converters authors [2] offer aqueous mixtures of different substances as working agents in secondary circuit of SPP (binary power plant). Advantage of mixtures in comparing with pure substances is possibility of controlling of their critical parameters by changing composition of components.

In this work, on the base of our own precised experimental data on $p, \rho, T, x$ -relations [3] thermodynamic properties and energy parameters of water–1-propanol binary mixture of different composition in the wide diapason of parameters, including critical and supercritical regions are determined.

To assess energy efficiency of the steam-turbine plant [4] we made a calculation of the water and water + 1-propanol cycles at the same conditions: pressure and temperature on turbine entrance are $p_1=16$ MPa and $T_1=623.15$ K; temperature of the steam in condenser $T_2=403.15$ K; coefficient of efficiency of the steam boiler $\eta_b=0.91$; inner relative coefficient of efficiency of the turbine $\eta_T^{\text{r}}=0.88$; inner relative coefficient of efficiency of the pump $\eta_P^{\text{r}}=0.85$; mechanical coefficient of efficiency $\eta_M=0.99$; coefficient of efficiency of electric generator $\eta_G=0.98$. As one can see on fig. 1, at the same thermobaric conditions (623.15 K and 16 MPa) water steam is saturated, but water + 1-propanol mixtures are at supercritical regions. The results of calculation are given on table 1 and demonstrated on fig. 2.
As one can see (fig.2 and table 1) thermal and effective coefficient of efficiency of SPP of water–1-propanol binary mixture in crease with 1-propanol concentration and reaches the maximum at $x=0.2$. With further increasing of 1-propanol concentration coefficient of efficiency decreases and at $x\to0.4$ it approaches to coefficient factor of water cycle of SPP.

Table 1. Values of coefficient of efficiency for the cycles with water and the water + 1-propanol mixtures ($x = 0.2, 0.5, 0.8$ mol. fractions of alcohol)

<table>
<thead>
<tr>
<th>Working substance</th>
<th>water</th>
<th>water+1-propanol, $x=0.2$</th>
<th>water+1-propanol, $x=0.5$</th>
<th>water+1-propanol, $x=0.8$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermal coefficient of efficiency $\eta_t$ (%)</td>
<td>24.4</td>
<td>27.6</td>
<td>22.9</td>
<td>20.9</td>
</tr>
<tr>
<td>Inner coefficient of efficiency $\eta_i$ (%)</td>
<td>21.3</td>
<td>23.9</td>
<td>19.7</td>
<td>17.8</td>
</tr>
<tr>
<td>Effective coefficient of efficiency $\eta_e$ (%)</td>
<td>18.7</td>
<td>21</td>
<td>17.2</td>
<td>15.7</td>
</tr>
</tbody>
</table>

As one can see thermal and effective coefficient of efficiency of the steam-turbine plant on water+1-propanol increases with concentration of 1-propanol and reaches its maximum at $x=0.2$ mol. fraction of alcohol. Further rising of concentration of 1-propanol leads to decreasing of efficiency.

There by, using water+1-propanol mixture (0.2 mol. fraction of 1-propanol) instead of pure water allows to:

1. decrease lower limit of operating temperatures to 50 K;
2. increase effective coefficient of efficiency;
3. partially unify thermal mechanical equipment of power plant, that iseconomically rational.

Литература:
Oxidative dehydrogenation of propane in the presence of CO$_2$ is a promising way to obtain propylene. The use of CO$_2$ as a mild oxidizer in the propane dehydrogenation reaction solves the problem of CO$_2$ utilization, which is one of the main greenhouse gases. At present, catalytic reactions under supercritical conditions are of great interest. The unlimited mutual solubility and high density characteristic of supercritical fluid contribute to the increase of catalyst productivity and dissolution of the compaction products deactivating the catalyst and their removal from the catalyst surface, which increases the lifetime of the catalyst.

Propane dehydrogenation in the presence of CO$_2$ under supercritical conditions was carried out on a 3% Cr/SiO$_2$ catalyst at a temperature of 600°C. The dependence of the activity and selectivity of the products on the ratio C$_3$H$_8$:CO$_2$ in the mixture, the propylene and olefin productivity were maximal at the ratio C$_3$H$_8$:CO$_2$= 1:4. A further increase in CO$_2$ in the reaction mixture leads to a decrease in propylene productivity and in the amount of olefins. The dependence of the output of the target product of the reaction on the rate of flow of reagents is revealed. When the C$_3$H$_8$+CO$_2$ mixture is fed at a rate of 1.3 mmol/min, its conversion reaches 70%, but a further increase in the flow rate leads to a decrease in the propane conversion. With an increase in the C$_3$H$_8$:CO$_2$ mixture feed rate from 1.3 mmol/min to 5 mmol/min, the selectivity for propylene increases and reaches 35%, and after a further increase in the propane feed rate to 10 mmol/min, there is a slight decrease in the propylene selectivity.

It is found that carrying out the reaction under supercritical conditions leads to an increase in the propylene productivity by 3 times and olefin productivity by 5 times compared with the reaction in the gas phase.
Heterogeneous hydrogenation of carbon dioxide is a way to obtain valuable chemicals: carbon monoxide, methane, hydrocarbons, alcohols or dimethyl ether [1]. Reaction direction and products distribution depend on chosen catalyst type. CO₂ hydrogenation over Fe-based catalysts leads to formation of hydrocarbons mixture. It is a two-stage process: reverse water-gas shift reaction followed by hydrocarbons synthesis of carbon monoxide and hydrogen.

Conduction of heterogeneous reaction under supercritical conditions can provide positive influence on activity and selectivity of the catalyst [2]. It is interesting to conduct the reaction in gas phase and under supercritical conditions to investigate influence of supercritical media on catalyst activity and products distribution. Hydrogenation was conducted over Fe/C, FeK/C and FeCuK/C catalysts, carbon material Sibunit was used as a support. Catalysts were examined with TPR, SEM, TEM and XRD methods. Activity tests were made in flow-type set up at temperature range of 250-400 °C and pressure 1-85 atm.

Critical parameters of H₂:CO₂ mixture were calculated with REFPROP 8.0. For ratio H₂:CO₂ = 1:1 they were: $T_k = 168,6$ K, $P_k = 4,48$ MPa. Reaction parameters 85 atm and 250-400 °C are related to supercritical conditions, 1 and 20 atm, 250-400 °C – to gas phase. Temperature range of 350-400 °C was chosen experimentally. At reaction temperature of 250 °C are merely active – CO₂ conversion was less than 3 %.

Pressure enhancement had a significant effect on products distribution (table 1). In gas phase at 1 atm over all catalysts reverse water-gas shift reaction prevailed with CO selectivity up to 98 %. Pressure increase led to growth of hydrocarbons ratio in reaction products.
Table 1 – Products of CO₂ hydrogenation (T = 350 °C, H₂:CO₂ = 1:1)

<table>
<thead>
<tr>
<th></th>
<th>P, atm</th>
<th>K CO₂, %</th>
<th>S CO₂, %</th>
<th>S C₅H₁₂, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeK/C</td>
<td>1</td>
<td>13</td>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>12</td>
<td>93</td>
<td>7</td>
</tr>
<tr>
<td></td>
<td>85</td>
<td>13</td>
<td>76</td>
<td>24</td>
</tr>
<tr>
<td>FeCuK/C</td>
<td>1</td>
<td>8</td>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>14</td>
<td>85</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td>85</td>
<td>15</td>
<td>50</td>
<td>50</td>
</tr>
</tbody>
</table>

Product distribution correlated with Anderson-Schulz-Flory law. Chain growth probability α decreased in the row: FeCuK/C > FeK/C > Fe/C. Fe-based catalysts worked stable at 85 atm, activity tests were conducted by 8-hour cycles.

References:

HYDROGENATION OF CO\textsubscript{2} ON SUPPORTED Cu-Zn CATALYSTS IN SUB- AND SUPERCRITICAL CONDITIONS  

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CO\textsubscript{2} emissions into the atmosphere pose a significant environmental problem. An increase of CO\textsubscript{2} in the atmosphere has such negative effects on the environment as global warming and a change in the pH of the world's oceans [1]. Nevertheless, CO\textsubscript{2} can be a source of carbon in organic chemistry. One of the ways to utilize CO\textsubscript{2} is direct hydrogenation. The products of direct hydrogenation of CO\textsubscript{2} can be olefins, alcohols, acids or CO, which can later be used to synthesize a wide range of organic compounds [2]. In this work, methanol was chosen as the target reaction product. Cu-Zn catalysts are often used for the CO\textsubscript{2} conversion to methanol at moderate temperatures (up to 300) and pressures (10-50 bar). However, this reaction has several disadvantages; some of them are the low productivity of catalysts and deactivation of the latter by the reaction products. Carrying out this catalytic reaction under supercritical conditions could solve these problems [2, 3]. The high density of the supercritical medium significantly increases heat and mass transfer, along with an increase in the solubility of the reaction products, which has a positive effect on the lifetime of the catalyst. The aim of the work is to study the hydrogenation of CO\textsubscript{2} on Cu-Zn catalysts containing 1–6\% mass. of metals on various oxide supports (SiO\textsubscript{2}, Al\textsubscript{2}O\textsubscript{3}, SiO\textsubscript{2}, ZrO\textsubscript{2}, MCM-41, etc., and their combination). The reaction was studied in a wide range of temperatures and pressures, including supercritical conditions. It has been shown that an increase in copper in the catalyst composition leads to an increase in CO\textsubscript{2} conversion. CO\textsubscript{2} conversion and methanol selectivity increase significantly with
increasing pressure to supercritical. The addition of SiO$_2$ into Al$_2$O$_3$ has a positive effect on the methanol yield. The catalysts were studied by various physicochemical methods (DSC-TG, XRD, UV-VIS, N$_2$ adsorption, SEM, TEM) before and after the reaction.


ORY-17

STUDY OF THE KINETIC REGULARITIES OF METHANE DRY REFORMING REACTION OVER NICKEL-CONTAINING CERIA-ZIRCONIA OXIDES

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Introduction. The methane dry reforming reaction (MDR) is promising for greenhouse gases and fossil fuels utilization for further synthesis gas production [1]. It is worth noting that Ni-containing catalysts are attractive in MRD due to their high activity and low cost. However, the main disadvantages of such systems are instability to Ni sintering and high coke formation. The solution of the problem is Ni deposition on an oxide matrix with high oxygen mobility, such as CeₓZr₁₋ₓO₂ with a fluorite structure [2]. The preparation of the above oxides can be carried out in a number of ways, one of which is synthesis in supercritical alcohols in flow-through mode [3]. As a result, oxides with a high degree of crystallinity with the necessary homogeneity of the spatial distribution of elements can be formed.

The aim of the work was to study the catalytic properties of nanomaterials based on Ni-containing ceria-zirconia, prepared by supercritical synthesis and by the Pechini method followed by deposition of Ni and Cu/Co, in the MDR reaction.

Results and discussion. Solutions of cerium sulphate and zirconium butoxide in isopropyl alcohol were mixed with each other to obtain the desired Ce/Zr ratio and injected with a syringe pump into the mixer. Isopropanol was fed to the same mixer by a plunger pump at a speed 1.8 times faster than the feed rate of salts solution. The supercritical synthesis was carried out in a tubular flow reactor at a temperature of 400 °C and a pressure of 120-130 atm. The products of the interaction of salts with supercritical isopropanol (sc-iPrOH) were cooled in a heat exchanger, depressurized and collected in a storage tank. A decantation method was used to separate the solid product. The precipitate was dried and calcined at 600 °C for 2 hours. Ni and Co/Cu
was loaded on ceria-zirconia by incipient wetness impregnation with solutions of Ni(NO₃)₂, Co(NO₃)₂ and Cu(NO₃)₂ followed by drying at 100 °C and calcination for 1 hour at 700°C.

Using supercritical isopropanol, a series of catalysts was obtained: 5% Ni/Ce₀.₅Zr₀.₅O₂, 2.5% Ni-2.5% Co/Ce₀.₅Zr₀.₅O₂, and 2.5% Ni-2.5% Cu/Ce₀.₅Zr₀.₅O₂; as well as 5% Ni/Ce₀.₅Zr₀.₅O₂ reference sample was prepared by the Pechini method. The materials were characterized by a number of physicochemical methods (XRF, SEM, TEM, H₂-TPR).

The stability of the operation of the above catalysts in the MDR reaction for 3 hours at a contact time of 7.5 ms and a temperature of 700 °C was investigated, the initial reaction mixture: 15 vol.% CH₄ + 15 vol.% CO₂ + rest N₂.

Collective deposition of Co or Cu with Ni leads to a decrease in methane conversion over time. The TEM results showed that apparently coke formation and sintering of the deposited phase are the causes of low activity.

Methane conversion over the Ni-supercritical sample turned out to be the highest compared to the Ni-Pechini sample of a similar composition, which indicates the uniformity of the spatial distribution of the elements, which is achieved using supercritical isopropanol synthesis method.

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Technical lignin is a by-product of the production of cellulose and biofuels from plant raw materials. The structure of lignin suggests that it can be a valuable source of chemicals, particularly phenolics. But despite this, most of technologies consider lignin as a waste of production. Nowadays, active search for the optimal method for the depolymerization of lignins into valuable products is underway all over the world. There are a lot of such methods, among which the most common are pyrolysis, catalytic hydrogenolysis, base-catalyzed depolymerization, etc [1].

In recent years, the use of supercritical technology is believed to have positive effect on the depolymerization of lignin material to small molecules. Water, alcohols (methanol, ethanol), water-alcohol and water-phenol mixtures are most often used as solvents [2].

But, despite the amount of work in this field, the available knowledge is insufficient for understanding the process of lignin depolymerization under supercritical conditions; there is a need for more fundamental studies of the mechanism, kinetics and thermodynamics of biopolymer transformations and the most complete characterization of the resulting products.

The purpose of this work is to study the influence of various factors (temperature, reaction time) on the rate of the depolymerization process of lignin and the yield of low molecular weight aromatic compounds in supercritical isopropyl alcohol. The object of the research was alkaline lignin obtained in the course of soda delignification of spruce wood.

The processing of lignin under supercritical conditions was carried out at temperatures of 200, 300 and 350 °C for 30, 90 and 180 minutes. The maximum degree of lignin conversion was 64% when processed for 180 minutes at 350 °C.
Such methods as high resolution mass spectrometry and high performance liquid chromatography were applied to characterize the products of lignin destruction in supercritical solvents.

The molecular weight and polydispersity of the samples were determined by size exclusion chromatography. In the experiment with the maximum temperature, it was possible to reach a mass of 700 Da, which is 10 times less than the mass of the initial lignin. Varying the duration of the depolymerization process affects the value of molecular weights to a lesser extent.

The content of the main monomeric structures of lignin (vanillic acid, catechol, guaiacol, cresol, eugenol, vanillin and acetovanillone) was determined by the HPLC method in the samples. Based on the sum of these compounds it was observed that the concentration of phenolic compounds increased with increasing time and temperature. At the maximum temperature and 3-hour treatment, the highest concentration of monomeric structures was 68 mg/g, of which the concentrations of catechol and guaiacol were 24 and 27 mg / g, respectively. Besides, at 200 ° C, the concentration of vanillin increased with increasing of the duration of treatment, but at 350 ° C, this compound was inversely related. Acetovanillone has a similar correlation.

Thus, in the course of the research, the influence of temperature and duration of the experiment on the rate of the depolymerization process of lignin was studied. The optimal experimental conditions were determined at 350 ° C and 180 min, under which the maximum degree of conversion (64%) and a high yield of low molecular weight compounds are achieved.

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Phthalic acid esters or phthalates are substances which are widely used as plasticizers in the production of various polymeric materials for industrial, household, food and medical purposes. The toxicity of phthalates depends on their structure and physicochemical properties, for example, it decreases with increasing length of the alkyl chains. With acute exposure, phthalates are relatively safe, but under the conditions of prolonged intake, they, being estrogen mimetics, accumulate in human body and can lead to the development of chronic diseases. In this regard, the problem of the presence of phthalates in packaging and sanitary-hygienic grades of paper that are in direct contact with humans or foodstuffs is particularly relevant.

Existing methods for the determination of phthalates are based on the use of gas (GC) and high performance liquid chromatography (HPLC). The use of HPLC for the separation of phthalates with similar properties requires the use of gradient elution, which creates significant problems due to concentration of trace amounts of phthalates present in the used solvents, on the stationary phase and makes the analysis difficult to reproduce.

Problem solving is possible using supercritical fluid chromatography (SFC), which has specific selectivity and high efficiency of analyte separation. The development of an approach to the rapid determination of phthalates in papers by the SFC method was the aim of the present study.

To achieve this purpose, we used a combination of accelerated solvent extraction of paper with subcritical methanol, SFC separation on a reversed-phase sorbent and tandem mass spectrometric detection in the selected reaction monitoring mode with electrospray ionization of analytes, ensuring maximum selectivity and sensitivity of the analysis.
The experiments were carried out using a chromato-mass-spectrometric system consisting of an Acquity UPC² SFC system (Waters, USA), a chromatographic pump for introducing an make-up solvent (Thermo, USA), and a 3200 QTrap hybrid triple-mass analyzer (ABSciex, Canada). Liquid extraction under pressure was carried out using the accelerated solvent extraction system ASE-350 (Dionex, USA). Carbon dioxide (grade 4.0, 99.99%) and methanol (LiChrosolv HPLC grade, Merck, Germany) were used as the mobile phase components. Methanol was also used as an extragent.

The test objects were used dimethyl phthalate (DMP), diethyl phthalate (DEP), dipropyl phthalate (DPP), diisopropyl phthalate (DiPP), dibutyl phthalate (DBP), diisobutyl phthalate (DiBP), benzylbutyl phthalate (BBP), diphenyl phthalate (DPhP), di-n-octyl phthalate (DNOP) and bis (2-ethylhexyl) phthalate (DEHP).

The study of analyte retention on various stationary phases under the SFC conditions and the influence on the separation of various parameters (flow rate and composition of the mobile phase, back pressure, temperature), as well as electrospray ionization processes of analytes in the presence of carbon dioxide, made it possible to optimize chromatographic analysis conditions. The developed approach allows the determination of ten major representatives of phthalates in 5 minutes with the lower limits of quantitative determination at the level of 1.0-5.0 µg /L using the isocratic elution mode.

Taking into account the stage of sample preparation by accelerated solvent extraction, the total duration of the analytical cycle in the study of paper samples did not exceed 40 minutes.

The developed approach was validated and successfully tested on a number of samples of packaging paper and cardboard, as well as toilet paper, in which the following phthalates were determined: DMP, DEP - 0.2 ± 0.1 mg / kg, DBP - 10 ± 5 mg / kg, DiBP - 4.0 ± 2.0 mg / kg, DEHP - 15 ± 5 mg / kg.

Research work was performed in the Arktika Core Facility Center of the Northern (Arctic) Federal University under support of the Ministry of Education and Science of the Russian Federation.
In the Republic of Dagestan, about 170 thousand tons of grapes are grown annually. Approximately 120 thousand tons of technical grape varieties are used to make wines and brandies. Grape marc together with grape seeds, the masses of which make up to 25 and 5%, respectively, of the mass of the grapes processed, are waste products of the industrial production of wine materials, and are practically not used in the republic. Depending on the variety and place of growth of the grape seed, the bones contain 8-20 wt. % fatty oil.

A promising technology for extracting fatty oil from wine grape seeds is supercritical fluid extraction with carbon dioxide (SCFE-CO₂), which provides a high degree of oil extraction and, at the same time, is free from drawbacks caused by the need to distill toxic solvent. Carbon dioxide has low critical parameters: T_{crit} = 30.9 °C, P_{crit} = 72.8 atm, critical density 0.469 g / cm³; CO₂ is not combustible and non-toxic, it allows for selective and in-depth processing of raw materials, varying the parameters of extraction.

As a research object, a mixture of grape seeds was used, obtained in late September 2018 from the ZAO Izberbashky Wine and Cognac Plant of the Republic of Dagestan.

The SKFE-CO₂ process was performed using a laboratory extraction system: model SFE 1000M1-2 FMS 50 manufactured by the company Waters Corp.

The numerical indicators of grape oil samples were determined by the methods of [1] using a spectrophotometer SPEC-RD 210 Plus.

From the data presented in the figure, it can be seen that increasing the pressure of CO₂ from 25 to 35 MPa at 30 °C leads to an increase in the yield of the extract from grape seed from 8.6 to 14.0 wt. %, i.e. 1.6 times, which is associated with an increase
in the density of supercritical CO$_2$ and, accordingly, its dissolving ability. A further increase in pressure from 35 to 45 MPa and an extraction temperature from 30 to 60 °C leads to an increase in the yield of lipids to 17.5 wt. % due to the extraction, along with fatty oil (15.0 wt.%) and waxy substances (2.5 wt.%). It should be noted that increasing the pressure of CO$_2$ from 25 to 45 MPa leads to a more significant increase in the yield of the extract than raising the temperature from 30 to 60 °C at the same pressure.

As a result of the conducted research, the effect of carbon dioxide pressure, temperature and time on the efficiency of supercritical fluid extraction of fatty oil and wax from grape seed was revealed. Optimal conditions for obtaining high-quality unrefined grape oil for the food and pharmaceutical industry from grape seed CO$_2$-extraction were determined: temperature 30 °C, carbon dioxide pressure 350 atm., Time 60 minutes under these conditions, the oil yield was 14.0% [2, 3].

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SUPERCRITICAL FLUID CHROMATOGRAPHY AS A TOOL FOR STUDYING PROCESSES IN HIGH PRESSURE ENVIRONMENTS

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Studying such processes as dissolution, interfacial distribution, adsorption, chemical transformations, etc. often requires accurate measurement of component concentrations in a solution. When such processes take place under high pressure (in particular, in supercritical (SC) fluids), concentration measurement is often associated with difficulties that lead to a decrease in the accuracy of measurements or the impossibility of carrying them out. For example, according to reference data [1], the solubility of substances in SC CO\textsubscript{2}, obtained by various methods, can differ many times. In general, obtaining the exact concentration of a substance dissolved in a SCF can be quite problematic.

In this paper, a method is proposed that allows determining the concentrations of substances dissolved in SC media with high accuracy and speed. The schematic diagram of the installation is shown in Fig. 1. In essence, this installation is represented by a high-pressure vessel for carrying out the process under study with the possibility of sampling an aliquot of the medium to the loop of a supercritical fluid chromatograph for further analysis. The advantages of this method are minimal disturbance on the system's equilibrium in a vessel by sampling, the absence of necessity to transfer analytes to another solvent, high speed and accuracy of analysis.

This apparatus can be used in the following areas:

1. Measurement of the solubility of substances in the fluid phase.
2. Investigation of the materials adsorption characteristics during adsorption from the SC phase.
3. Measurement of solutes distribution parameters between immiscible phases with the participation of SCF.

4. Carrying out chemical reactions in SC media with online monitoring of the reaction mixture composition.

5. Direct qualitative and quantitative analysis of extractable components in SFE.

![Schematic diagram of the installation](image)

**Fig. 1 -** Schematic diagram of the installation:
1, 7 - CO₂ pumps; 2 - co-solvent pump; 3 - six-way sampling valve; 4 - chromatographic column; 5 - detector; 6 - back pressure regulator; 8 - high pressure reactor; 9 - sampling system.

The test of the unit's performance was carried out by dissolving various weights of caffeine and benzoic acid as model objects in the SC CO₂ with subsequent analysis of their concentration in the solution (using the spike recovery test). The maximum error under this type of work did not exceed 3%.

**Acknowledgments**

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The rapid development of chemical technologies, the emergence of new materials and technical solutions are increasingly making it economically feasible to carry out the processes in sub- and supercritical (SC) conditions. Supercritical fluid (SCF) technologies have already proven themselves in the synthesis of pharmaceuticals, biologically active substances, thermal insulating materials, etc. without loss of selectivity during a process. Among the large number of methods that use SCF for the synthesis of various functional materials, special attention should be paid to the method of deposition in the medium of supercritical CO₂ - antisolvent (Supercritical AntiSolvent - SAS). It’s well-known that the supercritical carbon dioxide (SC CO₂) is an attractive medium for various physicochemical processes due to its availability, low price, inertness, non-toxicity, safety, ease of recycling, and low critical parameters (Tc=303.9 K, Pc=7.38 MPa). It should also be noted that the SAS method allows us to obtain dispersed metal-containing systems without the use of salts of nitrates and, thus, to avoid the formation of a large number of waste. This makes the SAS method more environmentally friendly compared to traditional methods for the synthesis of catalysts (impregnation, precipitation, etc.), which corresponds to the main directions of "green chemistry" defined by Nouri in 2005 [1].

This paper presents the results on the application of new approaches for the synthesis of heterogeneous catalysts, which combine the traditional sol-gel technology and the SAS method. So, in work [2], we first proposed an original approach to the synthesis of metal catalysts, which consists in the co-precipitation of the precursors of the active metal phase and the oxide sol, for example, SiO₂. As was shown, this approach
allows us to increase the specific surface area of the catalyst active phase by more than 3 times. Further studies have demonstrated the wide possibilities and “flexibility” of the approach in terms of the synthesis of heterogeneous catalysts with a given structure and properties. In particular, in the work [3], in the face of Ni-Cu-containing catalysts, we showed that small changes in the water content in the precursor solution make it possible to control phase homogeneity and to avoid separation in a bimetallic system. A method was also proposed for obtaining stable mesoporous oxide Al-Si-containing systems with a narrow pore size distribution, which makes it possible to control the number of acid sites presented on the surface of oxide supports [4].

Thus, the proposed approaches allow to fundamentally expand the possibilities of the method of precipitation in a supercritical antisolvent medium for the synthesis of heterogeneous catalysts for various applications.

The study was carried out with the financial support of the Russian Foundation for Basic Research in the framework of research projects No 18-29-06022 and № 18-33-00659.
In the modern world, the chemical and petrochemical industry plays a significant role. With high production growth rates, the high amount of toxic emissions and wastewater is growing. As a result, resources are spent extremely uneconomically and serious environmental problems are formed. To solve this problem, it is very attractive to use the process of supercritical water oxidation (SCWO) for the disposal of wastewater containing stable, difficult to washable substances, as well as complex mixtures of organic substances. This is due to the fact that supercritical water is able to completely dissolve any organic compounds and oxygen [1]. Especially effective is the use of supercritical water oxidation for the disposal and disposal of toxic organic waste containing xenobiotics and non-biodegradable substances in supercritical water [2].

As part of solving the problem of utilization of an aqueous solution of industrial runoff of a multi-tonnage process of epoxidation of propylene produced by PJSC "Nizhnekamskneftekhim" at the TOT department of FSBEI HE "KNRTU", the process of oxidation of this drain was studied on an experimental installation of a SCVO flow type [3], using as an oxidizer - air oxygen. The test stream was subjected to oxidation in the temperature range of 673–873 K and pressures of 22–40 MPa with 20-fold dilution with distilled water. The composition of the industrial effluent, which is an opaque emulsion with a strong odor, as well as the reaction products of the SCVO were determined by the chromatographic method (Table 1). Quantitative
and qualitative analysis was performed on a Flexar liquid chromatograph (PerkinElmer).

Table 1. Composition of industrial water runoff.

<table>
<thead>
<tr>
<th>Component</th>
<th>Component (mg/l)</th>
<th>Styrene</th>
<th>Ethylbenzene</th>
<th>Acetophenone</th>
<th>Methylphenylcarbinol</th>
<th>Phenol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Waste</td>
<td></td>
<td>92,588</td>
<td>0,046</td>
<td>2598,225</td>
<td>1449,3195</td>
<td>1256,640</td>
</tr>
<tr>
<td>Reaction product</td>
<td></td>
<td>1,550</td>
<td>&lt; 0,010</td>
<td>1,940</td>
<td>&lt; 1</td>
<td>&lt; 1,000</td>
</tr>
</tbody>
</table>

Studies have shown that by varying the temperature and concentration of reagents, it is possible to achieve almost complete utilization of toxic substances in a reasonable time [4, 5]. It is also worth noting that heat generation from the exothermic oxidation reaction of the components of the recyclable waste is an important component of the supercritical water oxidation process. This method has significant economic and environmental advantages compared with traditional methods of vapor-oxidation or combustion.

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Bibliography

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MODIFICATION OF NITROCELLULOSE IN SUPERCRITICAL CO$_2$

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An effective method of nitrocellulose (NC) modification by SAS procedure in supercritical carbon dioxide has been developed to obtain nanoscale spherical particles of NC and its composites containing carbon nanotubes (CNT) and iron oxide (III) (catalysts for ballistic powders combustion [1-2]).

![Fig. 1 – Structure and morphology of nitrocellulose: a) SEM image of the pure NC; b) SEM image of modified NC; c) TEM image of modified NC; d) particle size distribution of modified NC.](image)

The combustion tests of the fabricated samples have shown that the burning velocity of the modified NC is increased by 23% at the pressure below 2 MPa. The addition of Fe$_2$O$_3$ and CNT increases the burning velocity of the composites by 17-20% at a
moderately elevated pressure of 8-12 MPa. Moreover, the modified NC and its composites are characterized by a lower (up to 1,5 times) sensitivity to friction. Thus, for the first time the supercritical CO₂ medium has been used to obtain nanoscale particles of nitrocellulose and its various composites that demonstrate lower sensitivity to friction and higher burning velocity while maintaining their thermal stability. The proposed approach opens new prospects for the development of the well-known and new highly-efficient energetic compositions.

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Combustion of fossil fuels directly in the heat carrier increases ecological cleanness and energy efficiency of heat and electric energy production [1,2]. It is obvious that in order to develop new technologies based on combustion of different types of fuels in carbon dioxide, water vapor and supercritical water, it is necessary to identify combustion features of individual compounds in these media. Earlier we have studied the combustion of hydrogen, methane and isobutane in the nitrogen, carbon dioxide, and water vapor media [3−5]. The aim of the present work is to identify the effect of carbon dioxide and water vapor on propane, propene and isopropanol oxidation at elevated pressure of the reagents.

Experiments were conducted with the high-density fuel-enriched mixtures ($\rho_{\text{fuel}} = 0.22–0.25$ mol/dm$^3$, $\rho_{\text{O}_2} = 0.76–0.88$ mol/dm$^3$) diluted with argon, carbon dioxide, or water vapor (from 59 to 72% mol.) at the uniform heating (1 K/min) of tubular reactor to 640 K [6]. Proceeding on the time dependences of the reaction mixtures temperature increase caused by heat generation during fuel oxidation, it was found that the self-ignition temperature of propene is by $\approx 50$ K lower than propane in all the diluents and almost independent on diluent nature. The self-ignition temperature of isopropanol in the diluents increases in the following sequence: Ar < CO$_2$ < H$_2$O. The chain-thermal explosion was observed during propane oxidation in Ar and H$_2$O media, as well as during isopropanol oxidation in Ar and CO$_2$ media.

By means of mass spectrometric analysis, it was shown that propane oxidation in the CO$_2$ medium is characterized by a low degree of fuel conversion at almost complete consumption of O$_2$, while the propene oxidation is characterized by a low degree of O$_2$ consumption with a low degree of fuel conversion. This is consistent with the results of isobutane oxidation and explained by the high density of CO$_2$ and by the
presence of V–V resonances in the CO$_2$/hydrocarbon system [5, 6]. CO$_2$ dominates in the products of propane oxidation in the Ar medium, whereas methanol, acetone, acetaldehyde and acetic acid were found in significant amounts in propene oxidation products in the Ar medium. The isopropanol oxidation in the Ar medium is accompanied by intensive pyrolysis that is indicated by the high yield of H$_2$, CO and CH$_4$.

Fuels oxidation in the H$_2$O medium is accompanied by water evaporation and, as a consequence, increase in the reaction mixture heat capacity and thermal conductivity. During this process, a certain portion of the heat released upon fuel oxidation is spent on the water evaporation. It is shown that fuel oxidation in the water vapor medium occurs in several stages and is characterized by almost complete O$_2$ consumption in the reaction mixture. The high degree of fuels conversion in a water vapor medium can be caused not only by the chemical participation of H$_2$O molecules in elementary reactions but also by the vibrational excitation of O$_2$ molecules via the mechanism of resonant V–V exchange with H$_2$O molecules [3,5,6]. An insignificant amount of alkanes, alkenes, alcohols, aldehydes, and acids was detected in the oxidation products of propane and propene in the H$_2$O medium. Under conditions of water vapor low density, a high yield of H$_2$ was found during the propane oxidation, which was also observed during the isobutane oxidation [5]. Thus, the process of partial oxidation of alkanes in a water vapor media can be considered as an effective method of hydrogen generation.

In general, the results obtained indicate the diluents effect on the fuels oxidation not only due to a change in the reaction mixture heat capacity, but also as a result of the chemical participation of H$_2$O and CO$_2$ molecules in oxidation.

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SYNTHESIS OF SIMPLE AND COMPLEX OXIDES BY SUPERCritical ANTISOLVENT PRECIPITATION CO\textsubscript{2} TECHNIQUE

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In this paper, the authors were synthesized samples of simple oxides Al\textsubscript{2}O\textsubscript{3}, Fe\textsubscript{2}O\textsubscript{3}, Y\textsubscript{2}O\textsubscript{3}, NiO, Nd\textsubscript{2}O\textsubscript{3}, CaO, ZrO\textsubscript{2}, CoO and double oxides based on them via supercritical antisolvent precipitation CO\textsubscript{2} technique. These oxides are precursors in the manufacture of ceramics for various applications. Yttria-stabilized zirconia oxide ceramics (YSZ) are widely used in fuel cells and gas sensors [1], [2]. A ceramic based on CaZrO\textsubscript{3} is used in devices operating at elevated temperatures as a sensor for determining content oxygen, hydrogen and water [3]. In addition, calcium zirconate causes an increased interest as a material for microwave dielectric ceramics [4]. Iron-yttrium garnet Y\textsubscript{3}Fe\textsubscript{5}O\textsubscript{12} is a ferrimagnetic compound widely used in microwave and magneto-optical devices [5]. On catalysts with addition of zirconia and cobalt oxide as an active center it is possible the reduction of nitrogen oxides (I) [6].

The synthesis of powders was carried out on the experimental setup SAS 50 (Waters Corp.). Organic and inorganic salts were chosen as the starting salts: acetates (Ac), acetylacetonates (AcAc), lactates (Lac) and nitrates of the corresponding elements. Methanol (MeOH) and dimethylsulfoxide (DMSO) were used as solvents. The parameters of the experiments were varied in the following values: pressure 10-16 MPa, temperature 40-50 °C, feed rate of carbon dioxide (CO\textsubscript{2}) 35-50 g/min, feed rate of the initial solution 0.5-2 ml/min. The obtained samples were investigated by a complex of physicochemical methods: TG-DTA/DSC analysis, IR-spectroscopy, X-ray powder diffraction, transmission electron microscopy, X-ray photoelectron spectroscopy.

The synthesis in the environment of supercritical fluid CO\textsubscript{2} leads to the formation of stable products - nanoparticles of the corresponding metal salts in the X-ray amorphous state (Figure 1). When heated up to 200 - 450 °C organometallic
complexes are destroyed with the formation of X-ray amorphous simple oxides or, in a system of binary oxides, of a continuous series of X-ray amorphous solid solutions. With an increase in temperature, the phases crystallize with the decomposition of solid solutions in accordance with the phase relations of the well-known T – X diagrams.

Fig. 1 – The distribution map of elements in systems: (a) Zr(AcAc)-Co(AcAc), (b) Y(Ac)-Zr(AcAc), (c) Zr(AcAc)-Ca(Lac).

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INVESTIGATION OF THE MOLECULAR STRUCTURE OF ARBIDOL IN SUPERCRITICAL CARBON DIOXIDE BY NMR SPECTROSCOPY

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Arbidol (also known as umifenovir) is a synthetic antiviral drug developed over 30 years ago to combat the seasonal influenza virus [1]. Since that time, arbidol was shown to inhibit viruses from more than a dozen families [2]. Therefore, the study of the structure of Arbidol is a necessary step for developing a strategy for improving this compound, both in terms of biological activity and from the point of view of physicochemical characteristics. This problem is particularly relevant in the light of studies of the effect of supercritical solvents on the polymorphism of nanocrystalline forms of biologically active compounds in a polymer matrix. In this paper the features of the structure and spectral characteristics of Arbidol in scCO₂ and chloroform obtained using modern NMR methods are discussed.

The experimental data were obtained using the molecular fluid spectroscopy facility of G.A. Krestov Institute of Solution Chemistry, RAS (unique scientific equipment no. 503933). The reported study was funded by the Russian Foundation for Basic Research according to the project no. 18-29-06008. Also partial funding was provided by a grant from the President of the Russian Federation for state support of young Russian scientists – candidates of sciences: MK-1409.2019.3.


INVESTIGATION OF THE MOLECULAR STRUCTURE OF MEFENAMIC ACID IN SUPERCRITICAL CARBON DIOXIDE BY TWO-DIMENSIONAL NMR SPECTROSCOPY

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Polymorphism of biologically active compounds is a serious problem for the pharmaceutical industry because of its effect on the physical and chemical properties of solid powders. Therefore, the control of the polymorphism of medicinal compounds is a very important and urgent task. The compound possessing conformational polymorphism was chosen as the object of the study (mefenamic acid). Polymorphic forms of mefenamic acid show an enantiotropic transition, the transformation of form I into form II occurs at temperatures above 180°C [1]. Hence, a possible conversion to form II (metastable form) may jeopardize the stability of a pharmaceutical product and may change the effectiveness of the drug. Since the forms of mefenamic acid are determined by the molecular structure, it becomes necessary to investigate its structure in a critical state. This information will help to identify the nature of the nucleation of mefenamic acid. In the present work, the molecular structure of mefenamic acid was studied at supercritical state parameters by two-dimensional NMR spectroscopy.

The experimental data were obtained using the molecular fluid spectroscopy facility of G.A. Krestov Institute of Solution Chemistry, RAS (unique scientific equipment no. 503933). The reported study was funded by the Russian Foundation for Basic Research according to the project no. 18-03-00255. Partial funding was provided by a grant from the President of the Russian Federation for state support of young Russian scientists – candidates of sciences: MK-1409.2019.3.

Determination of preferred conformation of mefenamic acid in DMSO by
NMR spectroscopy and GIAO calculation, AIP Conference Proceedings, 2019 2063, 040007.
LEMS (laser engineering of microbial systems) is a promising technique, which is intended to be used for separation of small volumes of substance and living cells. This technique is based on the laser-induced forward transfer: pulsed laser radiation is focused on a thin metal coating on a glass substrate uniformly covered with gel containing microorganisms or soil particles [1]. The absorption of radiation leads to the local, intense and rapid metal and gel heating resulting into the film partial evaporation, and into the formation of a fast-growing vapor bubble and a micro-jet of liquid [2]. This jet transfers micro-droplets onto an acceptor glass plate. These droplets contain small volumes of soil or even single microorganisms, what increases the probability of separation of specific microorganisms. As it is shown in [3], LEMS has several advantages over the standard method of separation. Firstly, samples do not require preliminary preparation (extraction of living cells from mixed-phase and preparation of a liquid-phase sample). Secondly, this approach allows maintaining synergistic relationships and vitality of microorganisms, which are hard to cultivate, or which have not been cultivated yet.

The interaction of powerful pulsed laser radiation with a thin layer of metal leads to the formation of critical conditions of substance. This leads to a strong local increase of pressure and temperature, and to the ejection of metallic micro- and nanoparticles. Such processes can have strong negative impact on a transfer of microscopic living systems.

To assess these conditions by study of acoustic response of the system, an experiment (Fig. 1) and numerical simulations were carried out. The obtained results are used to
estimate temperatures and pressures arising in the processes of gel micro-droplets printing. This is required for clarification of the model of the physical processes, and for optimization of the system to minimize negative factors affecting living systems.

Figure 1. The outline of the experimental setup for registration of acoustic radiation. 1 – laser radiation, 2 – excited acoustic beam.

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**Literature**


A NEW METHOD FOR MEASURING SOLUBILITY IN MULTI-COMPONENT SUPERCritical FLUIDS USING COMBINATION OF SUPercritical ANTISOLVENT PRECIPITATION AND SUPercritical FLUID CHROMATOGRAPHY

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A task of solubility measurement in supercritical fluids is actual for many separation and particle formation processes using supercritical fluids, such as extraction, chromatography, micronization etc. The difficulty of this task is that media, in which measurement is carried out, exists only at high pressure. This fact makes impossible to use standard sampling technique. The main problem of current methods is that they are very time-consuming.

In this work, we propose new method for measuring solubility of low molecular weight polar compounds in supercritical fluids, based on combination of supercritical antisolvent precipitation (SAS) and supercritical fluid chromatography (SFC). The verification of this method is performed successfully. The validation is based on comparison of aspirin solubility in bicomponent fluids data, which were obtained using dynamic gravimetric method, with our data. Solubility measurements were carried out using CO₂ – acetone, CO₂ – methanol and CO₂ - ethanol mixtures in wide range of pressures and temperatures. Obtained results are close to literature data. That fact proves the validity of our method. The method allows gaining large sets of data in a short period of time and can be recommended for tasks where rapid assessment of solubility in supercritical fluids is required, for example, in SAS precipitation.

The work was financially supported by Russian Science Foundation, grant No. 17-73-20377.
One of the actual tasks of modern pharmaceuticals is the development of medicinal forms with enhanced bioavailability. Arbidol (umifenovir) is practically insoluble in water and, as a result, has a low bioavailability. One of the ways to solve this problem is developing a medicinal form of arbidol with enhanced solubility in water. One of these approaches is the synthesis of arbidol cocrysalts with other biologically active compounds (e.g. salicylic acid).

The method of supercritical anti-solvent sedimentation (SAS) is well suited for conducting rapid screening of various crystallization conditions for pharmaceutical substances, including the search for optimal conditions for obtaining cocrystals [1]. All experiments on supercritical anti-solvent sedimentation were performed using a SAS/RESS equipment manufactured by Waters Corp. The obtained substances were analyzed using DSC, TGA, microscopy and XPD analysis.

The results of the XPD analysis show that the micronized powder obtained during the SAS experiment has a high degree of crystallinity. In comparison with the diffractograms of the initial compounds, the formation of new peaks that characterize the formation of a new crystalline structure is clearly observed.

Comparison of the obtained microcrystals diffractograms with the diffraction pattern taken from the literature data [2] shows a good match between them. During the SAS process, umifenovir cocrystal with salicylic acid, umifenovir salicylate, was obtained.


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Currently, one of the most actual tasks is the developing of composite materials for sensors. Due to its high porosity and hardness, mesoporous silica is a unique matrix for the manufacture of gas sensors of various types. First of all, the difficulty of obtaining such materials is associated with the problem of drying conditions supporting the formation of spatial structure with high porosity.

Nowadays, the sol-gel method has been widely developed for production of new generation materials. Such method allows developing synthetic materials with new specific properties, controlled pore size, specific surface area, etc. Composite materials can be obtained both directly in the process of sol-gel synthesis, and subsequent processing of the obtained porous materials.

Drying is crucial stage for the formation of stable pores in mesoporous materials if they are obtained by the sol-gel method. During conventional drying, large stresses take place in the pores of the samples, which are associated with surface tension at the liquid – gas interface. The action of these forces in the drying process leads to the deformation of the cavities, and sometimes to the destruction of materials [1]. Drying under supercritical conditions is the way to solve these problems [2].

To study the properties and structure of the synthesized mesoporous samples and the obtained porous materials, electron microscopy, X-ray diffraction, and Raman spectroscopy were used.

During the work, mesoporous matrices of amorphous SiO₂ were obtained. They have an open net of interconnected pores and allow their infiltration with suspensions containing single-walled carbon nanotubes [3-5] for obtaining composite materials and gas sensors.
As a result of the work, a drying in the supercritical carbon dioxide and supercritical ethanol was developed and successfully tested. Obtained material can be used as the basis for the production of various composite materials and sensors.


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DEGRADATION OF ALIPHATIC POLYESTERS SCAFFOLDS
FABRICATED BY SUPERCRITICAL CARBON DIOXIDE FOAMING

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Supercritical fluid (SCF) technologies allow carrying out a wide variety of physicochemical processes, among which the fabrication of scaffolds from partially crystalline and amorphous biocompatible polymeric materials in the supercritical carbon dioxide (scCO$_2$) takes a special place. By varying the processing conditions, it is possible to form structures with the necessary architecture and porosity, which in turn allow to solve various problems associated with the development and creation of products for regenerative medicine. Along with high efficiency and reasonable price, SCF technology makes it possible to form the structures described above without the use of toxic organic solvents, as well as encapsulate various biologically active substances into them, which contributes to an increase in the biofunctionality of the products being formed.

One of the urgent tasks of regenerative medicine is the development and creation of tissue-engineering constructs (TEC) based on a fully resorbable plastic material to replace damaged and/or lost body tissues. Polymers of a homologous series of aliphatic polyesters that have the best biological compatibility among synthetic biodegradable polymers are often used as such material. When forming a TEC based on such polymers, to ensure the desired properties of the finished product, it is necessary to take into account the mechanism of degradation of these polyesters. It is known that there are two types of degradation which undergo in an aqueous medium polymeric structures at once: surface hydrolytic, as well as bulk autocatalytic degradation. The rate of polymer degradation is significantly influenced by the pH of the environment. When pH increases the rate of degradation decreases while improving system stability, and during acidification, the rate increases.

There are ester bonds along the surface of the polymer scaffold. In the case of surface hydrolytic degradation, these ester bonds are randomly hydrolyzed, which leads to
the release of polymer chains into the bulk of the medium, and, accordingly, to a decrease in the molecular weight of the polymer itself. At the same time, the hydrolysis products diffuse from the volume of the polymer scaffold and then are neutralized by a large amount of buffer present on its surface. During autocatalytic degradation, “acidic” hydrolysis products (monomers and low molecular weight oligomers) remain inside the volume of the polymer scaffold, which ultimately leads to the formation of acidified microenvironment and, accordingly, an increase in the rate of degradation.

The report presents the results of the study of the degradation rate of the surface and the internal volume of porous polymer scaffolds based on D, L-polylactide formed using SCFT in a Phosphate-buffered saline (PBS) solution for five weeks. The data obtained make it possible to build a mathematical model to predict the rate of degradation of the polymer scaffold, depending on its structure and morphology.

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Supercritical solvents are widely used in the processes of separation (extraction) of biologically active substances [1]. Since the conduct of such processes is directly related to the data on solubility, it becomes necessary to apply theoretical methods that would allow one to describe and predict the solubility of nonelectrolytes in mixed supercritical solvents. This work presents the results of a theoretical study of the effect of co-solvents (acetone and methanol) on the solubility of the biologically active compound – mefenamic acid (MA) in supercritical carbon dioxide (scCO₂) within the model of a athermal associated solution ASL (Associated Solution + Lattice) [2-4]. In this model, the expression for the deviation of solubility from additivity contains three contributions. 1. The combinatorial contribution takes into account the difference in the size of the molecules of the mixture components. 2. The chemical contribution takes into account the molecular association of the components of the mixture and is calculated on the basis of the theory of molecular association. 3. The calculation of the residual contribution that takes into account universal intermolecular interactions is performed on the basis of a simple lattice model. The model parameters are association reaction constants, the characteristic sizes of the molecules of the mixture components, and the binary interaction parameters. To calculate the solubility in a mixed solvent, data on the solubility of MA in pure acetone and methanol by isothermal saturation method with a gravimetric method for determining the concentration of a solute were obtained. The data on the solubility of MA in scCO₂ were taken from [1].
This work was supported by the Russian Foundation for Basic Research (grant № 18-03-00255-A).


CONFORMATIONAL MANIFOLD OF CARBAMAZEPINE IN SUPERCritical CO₂. MOLECULAR DYNAMICS SIMULATIONS.

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Polymorphism refers to a number of the most important characteristics of drug compounds. The ability of the active pharmaceutical ingredient (API) to exist in the form of more than one polymorph leads to the possibility of a situation in which one crystalline form can have a suitable dissolution rate, solubility and absorption, while the other is ineffective or even has side effects. Therefore, it is now very important to understand the factors contributing to polymorphism. One of the manifestations of polymorphism is the conformational diversity of the drug compound. In the present work, the conformational variety of the carbamazepine molecule was studied. Carbamazepine is used as an anticonvulsant drug in the treatment of epilepsy and trigeminal neuralgia. In the present work, the molecular-dynamic simulation of carbamazepine in supercritical CO₂ was carried out in a wide range of state parameters. In order to study the conformational diversity of carbamazepine, the metadynamics method was used.

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A polymorphism is an ability of compounds in a solid state to form more than one crystalline structure. This property essentially important value for production of dosage forms. The polymorphism affects a set of chemical and physical properties of biologically active compounds, including stability, solubility, efficiency (bioactivity) and also speed of dissolution and, therefore, bioavailability. One of the signs indicating conformational polymorphism is the conformational manifold of drug compounds. The conformational manifold of mefenamic acid was studied in the present work.

Mefenamic acid is a nonsteroidal anti-inflammatory drug from the group of fenamat, it has analgesic, anti-inflammatory and antipyretic effects. It can also be used in the treatment of cancer as a drug that stimulates the synthesis of endogenous interferon. Molecular dynamics simulations of mefenamic acid in supercritical CO$_2$ performed in the present work. The simulation was carried out along the isochore corresponding to a CO$_2$ density equal to 1.1ρ$_{cr}$ (CO$_2$) in a wide range of state parameters. The conformational manifold of mefenamic acid was studied by the metadynamics method. The results of this study are discussed in the report.

This work was supported by the RFBR projects № 18-29-06008 and the state task (registration number 01201260481).
Here we demonstrate a one-step laser method for creating materials with embedded catalytic hydrogenation NPs in scCO₂ media and an experimental setup for its realisation. The process of accumulation and deposition of NPs during laser ablation in a high-pressure reactor is observed in real time by optical absorption spectrum.

The advantages of using scCO₂ as a transport media for NP are discussed. The efficiency of the presented method is illustrated by electron microscopy data. The possibilities of this approach for creation nanocomposite materials with various combinations of NPs and their application are analyzed.
AORTIC VALVE DECELLULARIZATION IN scCO$_2$

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At the moment there is an increase in the number of patients with terminal stage of aortic valve of the heart disease requiring prosthetics. However, the exiting valve mechanical and biological prostheses have several disadvantages: lifelong anticoagulation to minimize the risk of thrombosis and embolism and also flagility which limits their use in clinical practice [1, 2]. The most promising direction for solving these issues is tissue engineering. In particular, the method of decellularization is one of the universal methods of obtaining low immunogenic cell-free matrices of various organ and tissue.

In recent years, the method of extraction in supercritical carbon dioxide (scCO$_2$) has become a new instrument for decellularization [3, 4]. scCO$_2$ is non-flammable, non-toxic, relatively inert in chemical processes. Also it has the desired properties of the solvent at relatively low pressure (7.38 MPa) and temperature (31.1°C).

In this work, was to use supercritical fluid for aortic valves were processed in the absence and presence of solvents. The effectiveness of the method was evaluated by histochemical staining (hematoxilin and eosin staining) and determination of the biomechanical properties of valves.

It was shown that alkali-salt treatment of samples during 1-1.5 hours with subsequent placement in scCO$_2$ fluid (t=37°C, P=15 mPa) contributed to the washing of cells from tissues. However, there was damage to the structure of the extracellular matrix (EM). The nuclei were conversed in the biomaterial during the process of
decellularization in scCO₂ fluid for 1 hour with the addition of an alcohol-water solution and different concentration of ethyl alcohol (from 30% to 64%). 

The hybrid detergent solution (24 hours)/scCO₂ (t=37°C, P=15-25 MPa, 3 hours) treatment of aortic valves cells were removed and the matrix structure was preserved. Mechanical tests showed a slight increase in young's modulus, maximum stress and maximum elongation in the treated tissue compared to the native one. Thus, combined treatment (detergent + environment SC-CO₂) allows to obtain cell-free intact matrix.

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**References**


In present work the conformational equilibria of carbamazepine molecules dilute in supercritical carbon dioxide being in equilibrium with the crystalline phase of carbamazepine under isochoric heating conditions were studied. Two isochores corresponding to the densities of CO$_2$ equal 1.1 and 1.3 of its critical density in the temperature range of 60°C–200°C were considered. The pressures ranges for these isochores were 131–419 bar and 151–539 bar, respectively. In this work, we applied an approach developed by us earlier. The main idea of this approach is the following. In order to monitor the polymorphic modification of pharmaceuticals the screening of conformational manifold of its molecules in supercritical fluid phase being in contact with solid phase is fulfilled. In its turn, to obtain the information on conformational manifold, the results of IR spectroscopy and that obtained within of quantum chemical calculations were used.

The successful application of this approach was demonstrated on the example of two pharmaceuticals possesses the different type of polymorphism, namely paracetamol (packaging polymorphism) [1] and ibuprofen (conformational polymorphism) [2]. The choice of carbamazepine as an object of inquiry was due to the fact that, in contrast to paracetamol and ibuprofen, it has a bigger number of polymorphic modifications possess both packaging and conformational types. Moreover, molecule of carbamazepine contains two benzene rings that are conjugated via central cyclic fragment. All this makes the aromatic system of the molecule conformationally not labile. The only conformationally labile fragment of the molecule is the carboxamide
fragment. Thus carbamazepine might be an interesting object to check the reliability of our methodology.

The IR spectra of carbamazepine diluted in supercritical carbon dioxide were recorded on the FTIR spectrometer Bruker Vertex80 in the wavenumber range of 1100–4000 cm\(^{-1}\) with resolution of 1 cm\(^{-1}\). The spectra were measured in temperature range of 60°C–200°C with step of 10°C.

Three spectral domains were chosen as analytical ones. These spectral ranges are related to the vibrations of aromatic system (1550–1640 cm\(^{-1}\)), to the stretching vibrations \(\text{C}=\text{O}\) (1650–1800 cm\(^{-1}\)) and \(\text{N}–\text{H}\) (3300–3500 cm\(^{-1}\)), respectively. An analysis of the spectral changes in these areas on the basis of quantum chemical calculations results allowed concluding the following.

1. In the temperature range of 60–110°C for two isochores the heating leads to a general increase in spectral intensity that corresponds to the increase of equilibrium concentration of carbamazepine in scCO\(_2\) phase. Along with this, a redistribution of the molar fractions of conformers (Conf. 1 and Conf. 2) is observed. It results in increase of the molar fraction of Conf. 2. In its turn the pressure increase also shifts equilibrium towards the Conf. 2 formation.

2. In the temperature range of 110–150°C the molar fraction of the Conf. 1 decreases and at the temperature of 140°C this value does not exceed the detection threshold. It was also found that at the temperature \(T=130°C\) tautomers of carbamazepine molecules appear in the CO\(_2\) phase. They are determined by proton transfer from the amide group to carbonyl oxygen. The further temperature increase shifts equilibrium towards their formation.

3. At temperatures of 160°C and 170°C, opalescence arises in the scCO\(_2\) phase and it is accompanied by the appearance of molecules of the iminostilbene protonated forms, which can presumably be formed due to the dissociation of carbamazepine molecules.

4. Consequent increase of temperature up to 180°C and further up to 200°C leads to disappearance of opalescence. At the same time, in the temperature range of 180–200°C the tautomers become the main structural units in the supercritical fluid solution.
The work was supported by the Ministry of science and high education of the Russian Federation (project № RFMEFI61618X0097).


In present work the conformational equilibria of mefenamic acid (MA) molecules in the supercritical carbon dioxide (scCO₂) phase were investigated. These studies were carried out for a solution with a MA concentration of ~10⁻⁴ of mole fractions under isochoric heating conditions. The isochore corresponding to the CO₂ densities equal 1.1 of its critical density in the temperature range of 140–210°C were studied. The pressure range for this segment of isochore was 296–439 bar.

Crystalline MA is characterized by conformational type of polymorphism and can exist in three polymorphic modifications. The first polymorph (Form I) is more stable and this form is used in the pharmaceutical industry. However, from the therapeutic point of view, the second polymorph (Form II) might be the more interesting due to its higher dissolution rate compared to the first form. This allows achieving the required concentration of active pharmaceutical ingredient in biological media for a shorter period of time. Thermal conversion of the first form is one of the ways to produce of polymorph II. Obtaining a third polymorphic form is not a trivial task, and therefore this polymorph will not be considered within this study. Taking into account the conformational type of MA polymorphism, its second polymorph can be obtained by crystallization from a supercritical solution containing corresponding conformers.

In this work, to screen the conformational manifold of MA molecules in the scCO₂ phase we applied an approach based on the analysis of the results of IR spectroscopy and quantum-chemical calculations. IR spectra of the binary mixture (MA–scCO₂) were measured in the wavenumbers range of 1100–4000 cm⁻¹ with resolution of 1 cm⁻¹. The spectra were recorded in temperature range of 140–200°C with step of 10°C.
Within applied approach a preliminary conformational search for MA molecules was carried out using quantum chemical calculations. For the found conformers, their energy characteristics, frequencies of functional groups vibrations, as well as the barriers of transitions between them were determined. Basing on the data obtained, the analytical spectral bands in the wavenumbers range of 1400–1550 cm\(^{-1}\) were chosen. These bands are related to complex vibrations that include vibrations of the aromatic system atoms and rocking vibrations of N–H group in MA molecule. Analysis of spectral changes in this spectral domain showed the following.

In the temperature range of 140–180°C conformer I dominates in the scCO\(_2\) phase and the ratios of molar fractions of two conformers remain to be almost constant. In the temperature range of 180–200°C, the jumplike redistribution of the molar fractions of these conformers occurs and conformer II becomes predominant in the scCO\(_2\) phase. Upon the further heating, the complete conformational transition was not achieved, and at the temperature T=210°C in scCO\(_2\) phase the conformer I concentration remained about 18% of mole fractions. It points on the higher stability of the conformer II at temperatures above 180°C with the comparison to conformer I. However, according to quantum chemical calculations the probability of this conformational transition is extremely low due to the high energy barrier (~ 50 kJ / mol). This contradiction is due to the fact that quantum-chemical calculations do not take the temperature into account when determining the energy characteristics (all calculations are performed for T=0 K). However the allowance of temperature must lead to a decrease of this energy barrier. This is linked to the significant increase of fluctuations of the atoms relatively their equilibrium position that leads to the increase of quantum conformational transition probability.

On the other hand, this conformational transition can be realized via the transferring of a hydroxyl proton onto carbonyl oxygen in the MA molecule. This proton transfer can occur either in a dimer of MA or in a complex formed between MA and molecules of environment. However, to find the answer for this question, it is required the performing the additional researches.

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LASER MICROSTRUCTURE OF TRANSPARENT OPTICAL MATERIALS IN THE MEDIUM OF SCF

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Optical and spectroscopic diagnostics of physico-chemical processes occurring in supercritical media is an urgent task for a wide range of studies. As a rule, such studies are carried out in special optical reactors that have two transparent high-pressure windows, which makes it possible to obtain information either by using spectroscopic instruments or by optical control. But, sometimes, to obtain more detailed information, it is necessary to use several channels of information at the same time — for example, to simultaneously visualize the process of polymer foaming in two projections, and also to probe the sample using laser radiation by multispectral diffusion-wave spectroscopy. For the implementation of such processes, the concept of a modular high-pressure reactor has been proposed, which allows us to largely adapt our design to solve a wide range of tasks related to the integrated optical diagnostics of various processes in situ. In the basic configuration, the reactor has 8 ports for optical access to the internal volume of the reactor.

With the help of a high-pressure reactor, a cycle of works was carried out to study the process of foaming plasticized polymer with a decrease in pressure of the plasticizing subcritical\SCF agent.

The work was financially supported by the Russian Foundation for Basic Research (project 18-29-06024 in terms of developing methods for controlling the foaming process of polymeric materials) and the Ministry of Science and Higher Education in the framework of the work on the State task of the FNIC Crystallography and Photonics of the Russian Academy of Sciences in terms of the development of supercritical fluid technologies.
SCF ENCAPSULATION OF LEVOFLOXACIN IN BIORESORBABLE POLYMERS AND STUDY OF ITS RELEASE KINETICS IN BUFFER SOLUTION

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At the present time controlled release drug formulations are widely used in medical practice, in particular, drugs encapsulated into bioresorbable polymeric matrixes. Fabrication of such polymer structures by supercritical fluid (SCF) technologies allows to avoid the use of toxic solvents and high temperature processes, which can negatively affect both the drugs and the polymer by changing its physical and chemical properties uncontrollably.

In the present work, two types of bioresorbable polymeric scaffolds encapsulated with levofloxacin (fluoroquinolone antibacterial drug) were formed using supercritical carbon dioxide (sc-CO₂): microparticles (5-20 microns) and porous cylinders (5 mm in height and 5 mm in diameter). Polylactoglycolide (Purasorb PDLG7502, Corbion Purac, the Netherlands) and levofloxacin (Sigma Aldrich, USA), which was encapsulated in a polymer in an amount of 10 wt.%, were used for polymeric structures formation. The microparticles were manufactured using the PGSS (Particles from Gas Saturated Solution) method at a temperature of 40°C, a pressure of 20.0 MPa and a residence time of the initial mixture in a high-pressure reactor - 1 hour. Porous cylinders were produced by the method of SCF plasticization and subsequent foaming. Mechanically grounded polylactoglycolide powder, mixed with 10 wt. % of levofloxacin, was plasticized in a cylindrical mold in sc-CO₂ at a temperature of 40°C and a pressure of 10.0 MPa for 1 hour. After that, the obtained mixture was foamed as a result of pressure release to the atmospheric value in the reactor.
To study the kinetics of release of levofloxacin from polymer matrixes, weighed samples of manufactured composite structures were placed in glass containers filled with phosphate-buffered saline (pH = 7.4), which were then placed in a thermostat shaker at 37°C. The release of levofloxacin from the polymer scaffolds starts from the surface of the polymer structure, and then from the inner regions due to its hydrolyze (degradation). The concentration of levofloxacin released into the solution, was measured using UV spectrophotometry (Cary 50 spectrophotometer, Varian, USA) at regular time intervals.

The kinetics of the levofloxacin release from polylactoglycolide microparticles and porous cylinders differed significantly. As concerns microparticles, a steep («burst») release of the medicine (about 80% of its total amount) was observed on the first day. Over the next day the microparticles were quickly degrading resulting in the release of the remaining 20% of levofloxacin. In the case of porous cylinders, the initial release was only 4-6% of the total amount of drug in the sample. After that, levofloxacin was gradually releasing over a period of three weeks at a rate of about 2-5% per day.

Thus, polymer microparticles and porous cylindrical scaffolds encapsulated with levofloxacin were formed by the of PGSS and SCF plasticization with subsequent foaming in sc-CO₂ methods. It was shown that the use of various parameters of SCF fabrication of controlled release levofloxacin components formulation based on bioreposable polymers allow to control the shape, size, porosity of the produced polymer structures, and the kinetics of drug release.

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Salicylic acid is an important aromatic oxoacid, which is widely used in the national economy. Salicylic acid has an anti-inflammatory effect and is used in the production of painkillers and antipyretics, including acetylsalicylic acid, methyl salicylic acid ether. Also, significant amounts of salicylic acid are used as a preservative in the food industry and in the preparation of feed for farm animals. In addition, salicylic acid is used in the production of azo dyes, as well as in the production of ester fragrances.

Currently, almost all salicylic acid production is carried out by the Kolbe-Schmitt method. The main technological feature of the Kolbe-Schmitt method is the return of up to half the amount of phenol during the reaction of sodium carboxylate and the formation of disodium of substituted salicylic acid. As a result of the above process, the maximum theoretical yield is 50% of the amount of sodium phenolate used. In addition, the residual phenol contaminates salicylic acid. A way to solve this problem is to use supercritical carbon dioxide as a reaction medium and reagent.

In this paper, salicylic acid was synthesized using supercritical carbon dioxide as a reagent. The influence of pressure, temperature, concentration of reagents, type of counterion on the process of phenol carboxylation in supercritical carbon dioxide was studied. The process was carried out in a high-pressure steel reactor PARR-4251 (Parr Instrument, USA). Previously, the synthesis of sodium or potassium phenolate was carried out by the interaction of phenol with sodium or potassium hydroxide with 5% excess. The synthesis was carried out for 2 hours at a temperature of 120 °C. After the temperature in the reactor was risen up to 180 °C, the refrigerator was opened and the water was distilled for 1 hour. In the future, for complete removal of water from the reaction mixture through the reactor was purged with nitrogen at a
flow rate of 20 mL/min for an hour. The pre-dried sodium or potassium phenolate in the reactor was heated to the required temperature (180-300 °C) and carbon dioxide the amount of which was measured by the dosing pump was fed into the reactor. The pressure in the system was regulated by a reducer. The reaction was carried out for 6 hours, with hourly sampling during the reaction. The amount of formed products and residual phenol was determined by HPLC method.

The study of the effect of temperature on the process of carboxylation showed that at a temperature of 180 °C for 6 hours, a 20% conversion of sodium phenolate is achieved. With an increase in temperature to 250 °C, there is an increase in conversion to 95% for 6 hours of the process. With a further increase in temperature to 280 °C, 95% of the substrate conversion is observed at the third hour of the carboxylation. With small conversions of sodium phenolate, the observed selectivity of the process for salicylic acid is 70-85%, with the main byproduct being p-oxybenzoic acid. Upon reaching the conversion of the sodium phenolate in the 90-98% is observed a sharp decrease in the selectivity of the process associated with further carboxylation of salicylic acid and the formation of 2.4 – dicarboxylate sodium.

The study of the pressure effect of carbon dioxide on the yield of salicylic acid showed that the increase in pressure of carbon dioxide increases the rate of the conversion of the phenolate of sodium, however, the increase in pressure has no noticeable effect on increasing the selectivity of the process of synthesis of salicylic acid. With the increase of conversion is observed a significant decrease in the selectivity of the process for salicylic acid from 87% to 60-65%, which indicates the occurrence of a parallel side of the process of formation of the p-carboxyphenyl sodium.

In the course of the study, the optimal conditions for the phenol carboxylation reaction were determined: \( t = 250 \, ^\circ C \), \( P_{CO_2} = 8.0 \) MPa, \( c(CO_2)/c(Phenol)=1.05 \).

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HIGH-PRESSURE REACTOR FOR EPR SPECTROSCOPY

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Polymer processing in supercritical fluid solvents is a promising field in polymer technology. It can be used to impregnate polymers with various low-molecular weight compounds: dyes, biologically active substances \textit{etc}. Electron paramagnetic resonance (EPR) spectroscopy in combination with the spin probe or spin label approaches is a powerful tool for investigation of materials and processes associated with them. Several important physicochemical parameters of the material can be determined by this method, such as the solubility or the swelling degree in different media, the bulk or local concentration of low-molecular weight dopants, the rotational and translational diffusion coefficients \textit{etc}. However, EPR spectra acquisition at high pressures sets some strong requirements for the design of the ampule and sample preparation. A few acquisition methods reported in the literature suffer from several serious drawbacks.

In the present study we propose a high-pressure reactor designed by our group for EPR spectra acquisition in liquids and supercritical fluids at elevated pressures and temperatures up to 80°С. The reactor consists of a polyetheretherketone (PEEK) ampule, a stainless steel body connected to a high-pressure line by a detachable joint, a pressure gauge and a thermocouple. For kinetic measurements the reactor can be attached to an auxiliary high-pressure vessel via a high-pressure valve.

The reactor was used to acquire the EPR spectra of a stable nitroxide radical TEMPON (4-oxo-2,2,6,6-tetramethylpiperidine-1-oxyl) in supercritical carbon dioxide and in ternary systems supercritical carbon dioxide-TEMPON-polylactide (or polycarbonate).

\textit{This work was supported by Russian Foundation for Basic Research (grants 17-02-00445 and 18-29-06059).}
SCF ENCAPSULATION OF SPIN PROBES TO STUDY THE PROCESS OF ALIPHATIC POLYESTERS HYDROLYSIS.

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Bioresorbable 3D structures – matrices formed for development and creation of tissue-engineering structures must simultaneously satisfy various physical, chemical and biological requirements, for example, in quality and speed of their biodegradation. It is also important to be able to control the distribution of various biologically active substances, diagnostic and medicinal agents encapsulated in such matrices. Modern techniques of SCF encapsulation of these ingredients into polymer structures using supercritical carbon dioxide (sc-CO\textsubscript{2}) allow these processes to be carried out at physiological (≤ 40 °C) temperatures, ensuring the preservation of the physical, chemical and biochemical properties of the starting components, without introducing any toxic components, which, of course, is relevant for various biomedical applications [1].

In our work, the fabrication of samples of the matrices under study was carried out on the basis of a bioresorbable copolymer of lactic and glycolic acids (poly (D,L-lactic-co-glycolic)) of the brand Purasorb PDLG 7502 (manufactured by Corbion Purac, Netherlands) and an EPR-active spin probe TEMPON (Sigma-Aldrich), that has high (more than 10-3 mol/l) solubility in sc-CO\textsubscript{2} under the conditions of our experiments. The original copolymer granules (1-3 mm in diameter) were ground by a rotary mill. The resulting powder was sieved through a set of sieves, and a fraction with a particle size of 50-100 microns was selected. A certain amount of TEMPON was placed at the bottom of the variable volume high-pressure chamber (2.5 mg for 52.9 ml and 5 mg, for 32.9 ml). A metal container with a copolymer powder of a mass of 0.377 g was placed upon. Then the high-pressure chamber was sealed and filled with carbon dioxide to the pressure of 12.0 MPa at a temperature of 41°C. The whole system was
kept in these conditions for 2 hours. After the SCF impregnation process was over, the release of CO\textsubscript{2} pressure to the atmospheric value occurred within 30 minutes. The obtained foam composite was ground in an agate mortar to obtain fine particles with a characteristic dimension of less than 100 microns. A special cylindrical mold and laboratory press PGR-10 was used for the fabrication of monolithic samples. 26 mg of copolymer particles with TEMPON was placed in a mold (area of 1 punch 0.2 cm\textsuperscript{2}), heated to \( T = 50 \degree C \) and pressed under a load of 6 tons. Pressing lasted 50 minutes. Pressure drop occurred at \( T = 29 \degree C \). After that, transparent (which indirectly indicated absence of macroscopic structural defects) discs with diameter of 5 mm and 1 mm thick were removed from the mold to further investigation of the process of their hydrolysis in phosphate-saline buffer solution using EPR spectroscopy.

This work was supported by the Ministry of Science and Higher Education in the framework of the work on the State task of the Federal Research Center for Crystallography and Photonics of the Russian Academy of Sciences in terms of developing the SCF impregnation process for aliphatic polyesters with spin probes and the Russian Foundation for Basic Research (Grant No. 16-29-07356) in developing a method for forming monolithic poly(D,L-lactic-co-glycolic) matrices, grants 18-29-06059 (Design and probe methods for diagnosing polymeric biomedical materials formed in the medium of supercritical carbon dioxide) and 17-02-00445 (EPR diagnostics of degraded polymeric structures containing biologically active substances).

SCF FABRICATION OF BIORESORBABLE POLYMERIC SCAFFOLDS FOR TARGETED DELIVERY OF GENTAMICIN

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Application of the principles of supercritical fluid (SCF) processing technologies for bioresorbable polymeric materials in supercritical carbon dioxide (sc-CO₂) for fabrication of structures of a given architectonics encapsulated with medicinal preparations is one of the most promising approaches for developing new controlled release drug formulations. The high diffusion rate, low viscosity, controlled dissolving power of SCF and the ability of complete removal of the solvent facilitate the fabrication of bioresorbable polymeric scaffolds uniformly filled with drugs, with desired morphology and a well-developed system of connected pores providing control of drug release kinetics. Initially it is determined by the diffusion rate of the encapsulated drug substances from the surface of the scaffold, and then from the inner regions due to its biodegradation (hydrolyze).

In the present work composite porous scaffolds and microparticles based on polylactoglycolide and gentamicin (broad-spectrum antibiotic) were formed using SCF technologies to provide the targeted delivery of bactericidal drugs to the tissues of the body and ensure their prolonged action. The method of Raman-scattering spectroscopy was used to investigate in vitro the kinetics of antibiotic release from bioresorbable polymer scaffolds and microparticles in phosphate-buffered saline. Studies showed that on the first day of the experiment almost 100% of gentamicin was released from polymer microparticles. At the same time, the release of gentamicin from polymer scaffolds for the first day was only 25-28%. After that, gentamicin was gradually releasing over a period of three weeks till the complete degradation of the scaffolds on the 22nd day.
Thus, it was shown that the use of the developed SCF methods allows to fabricate polymeric structures with a controlled rate of release of biologically active substances in the model physiological media.

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The anomalous decrease of the viscosity of water with applied pressure has been known for over a century [1-3]. It occurs concurrently with major structural changes. It is well-known [1-4], that the water structure is the tetrahedral nearest ordering due to the hydrogen bonding between water molecules. Viscosity is a macroscopic witness of the existing of the tetrahedral hydrogen bond network that makes water so peculiar. For liquid water at temperatures below 323 K, the viscosity decreases with increasing pressure although the density increases. Similar viscosity behavior is observed for near supercritical water under pressure below the critical temperature ($T_c=647.27$ K). Because of the anomalous behavior of the pressure dependence of the water viscosity, almost no quantitative descriptions have been proposed to determine the pressure or density dependence of the viscosity. For the prediction of the pressure dependence of viscosity of water only few models exist so far [3-5]. Some viscosity equations were based on the assumption that the viscosity depends on the molecular free volume. In other cases, the viscosity of water had been presented by empirical equations for the temperature and density dependences which contain adjustable coefficients without physical meaning. It was found that the relative deviations between measured data and data extracted from various equations were (3 to 30) % as described by authors of works [4,5].

We propose an approach that treats water as occurring in two states (liquid and steam), and explains its viscosity properties. As it is known, the two different mechanisms need to be considered for the viscous flow in various phase states. The first one, occurring in liquid, is well known as momentum transfer by intermolecular interactions between the dense packed molecules. The second one, as the temperature
increases very significantly, imply a momentum transfer by collision of the freely migrating molecules in the gaseous state. In the work, we presented two equations for the pressure viscosity behavior of liquid water in the temperature ranges (273 to 373) K and steam in the range (373 to 1023) K and pressures up to 100 MPa.

The equation (1) have been used to describe the molar fluidity isotherms of liquid water in the temperature range (273 to 373) K and pressure up to 100 MPa. The molar fluidity along each isotherm can be expressed as two-parameter regression equation:

\[ F_m(P) = a' + b_1' \cdot V_m(P) + b_2' \cdot D_w(P), \]  

(1)

where \( a', b_1' \), and \( b_2' \) are constants. The geometric descriptor, \( D_w = N_A V_w / V_m \) (where \( N_A \) is Avogadro number, \( V_w \) is van der Waals volume), is known as a molecular packing density in a liquid or a fluid [5]. \( D_w \) may be taken as some function of molecular specific interactions which depend on the structure of the liquid. The change of molecules packing is also a function of the pressure and temperature. It is noted that \( D_w \) values increase with pressure for the associated liquids and fluid studied.

The dependence of the molar viscosity for water steam in the range (373 to 1023) K and pressure up to 100 MPa can be given by the following expression:

\[ \eta_m(P) = q' + k_1' \cdot V_m(P) + k_2' \cdot D_w(P), \]  

(2)

where \( q', k_1' \), and \( k_2' \) are constants. Standard multiparameter regression analysis was used to obtain the coefficients of the equations (1) and (2). The equations (1) and (2) are validated by the values of correlation coefficient \( (r_{corr}) \), root mean square deviation \( (RMSD) \) for regression and \( F \)-distribution coefficient \( (F_{statictic}) \). A successful evaluation of the water viscosity was carried out over the range of pressure from 0.1 to 100 MPa and in the above temperature ranges. Thus, it was found that the coefficients of Eqs. (1), (2) are functions of temperatures and independent of pressure. For the water steam the values of coefficient \( k_1' \) in Eq. (2) increase linearly with increasing temperature from 373 to 1023 K. At the same time, the values of coefficient \( k_2' \) decrease with increasing temperature down to a minimum at near \( ~T_c \), but in the temperature range from 700 to 1023 K the slight growth of coefficient \( k_2' \) is observed for the water fluid.
The correlations between experimental viscosity of water and calculated one based on these models are quite significant. The equations (1) and (2) hold over the above regions with a very high precision. In the case of the liquid and fluid, the AAD (average absolute relative deviation) does not exceed 1.25 %, which is comparable to the accuracy of the viscosity experimental data.

References

SORPTION ACTIVITY OF A GRAPHENE/Fe₃O₄ SYNTHESIZED IN A SUPERCRITICAL ISOPROPANOL MEDIUM

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Novel materials, possessing unique chemical activity provided by a large number of open functional sites on the contact surface and having a developed transport pore system, a significant specific surface, and, at the same time, the required mechanical, physical and chemical characteristics, are the goal of studies of many world’s research teams working on the problem of developing highly efficient sorption materials for fine purification of aquatic media.

Developing aerogel materials based on graphene under supercritical conditions seems to be one of the most promising modern solutions. The preparation of aerogels intercalated or modified with active functional substances (for instance, nanoscale metal particles) is of particular interest. In the present paper, the authors describe a nanocomposite sorption material obtained by synthesizing a hydrogel, representing a graphene oxide (GO) aqueous paste modified with iron nanoparticles (GO/Fe₃O₄), through mixing a GO solution and iron (III) compounds in an aqueous-organic solvent and subsequent processing of the mixture at elevated temperature. Then, the hydrogel was converted to the aerogel form under conditions of supercritical drying in an isopropyl alcohol medium in an NMA 2005s high pressure autoclave (Nano-Magc Technologies Pvt. Ltd., Delhi, India). The resulting product represented a light black airgel possessing high magnetic properties, which indicates the reduction of iron(III) hydroxide precipitated on graphene to form magnetite.

Figure 1 shows scanning (SEM) and transmission (TEM) electron microscopy images of the structure of the sorption materials. The hydrogel (Fig. 1a) is characterized by the presence of graphene flakes forming the porous structure of the material. The supercritical drying of the sample (Fig. 1b) contributes to the formation of nanoscale iron particles with a diameter of 50-350 nm (due to the reduction of iron hydroxide).
Figure 1. SEM images of the dried hydrogel (a) and aerogel (b).

Figure 2. TEM image of the structure synthesized

In the present research, studies were conducted to determine the sorption activity of the obtained materials with respect to the model organic pollutant - methylene blue (MB) synthetic dye. The sorption capacity of the hydrogel, dried hydrogel and aerogel was found to be ~2500, ~1500 and ~2300 mg/g, respectively. Thus, it can be concluded that the graphene nanocomposite synthesized by the authors exhibits high sorption characteristics with respect to organic pollutants. The need to develop a sorption material in the operational form suitable for widespread use in conventional industrial sorption processes can be the most important rationale for the implementation of supercritical conditions for obtaining the aerogel form of the developed nanocomposite.

The work was performed within the framework of the project part of State Assignment No. 16.1384.2017/PCh of the Ministry of Science and Higher Education of the Russian Federation.
PECULIARITIES OF CARBON NANOTUBES TREATMENT VIA RAPID EXPANSION OF SUPERCRITICAL SUSPENSIONS


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Carbon nanotubes (CNT) are a carbon allotrope modification representing graphene sheets rolled into hollow cylindrical structures of various diameter and length. Individual CNTs possess unique optical and electrical characteristics which makes them desirable building blocks for various functional materials. Since their discovery in the 90-th of the XXth century methods of CNT-based materials formation are being developed and improved which would allow implementing CNT properties on a macroscopic level. The majority of these methods require suspending CNTs in a liquid at a certain process stage; at that, as a rule, maximum, preferable total de-agglomeration of CNTs in suspension is typically required. This result is difficult to achieve since CNT have a very strong intermolecular interaction potential towards each other. Usually de-agglomeration is performed using repetitive powerful ultrasonication and consecutive centrifugation. Main drawbacks of this method are high level of CNT destruction due to sonication and low CNT concentration in the suspension due to large losses at centrifugation.

There is a method of nanoparticle dispersing in liquids using gas-like supercritical fluids. Technically it is close to RESS method (Rapid Expansion of Supercritical Solutions) and is sometimes referred to with the same abbreviation. The method goes as follows: a disperse material is suspended in a fluid, and then the whole volume of the suspension is catastrophically sprayed into a collection vessel. The method is
used for processing various nanosized materials including CNT [1–3]. Spraying can be performed into an empty vessel [1–3] resulting in a powder with decreased bulk volume density and its consecutive suspension in a liquid using traditional approaches, as well as directly into liquid resulting in a concentrated suspension. In case of CNT this treatment allows increasing the degree of de-agglomeration and simultaneously diminish ultrasonication damage to CNTs by decreasing its power [3,4].

In this work, the effect of RESS process parameters on the properties of CNT powders and liquid suspensions is investigated. It was shown that in dry spraying (that is, spraying in to an empty collection vessel) fluid type has a major influence on bulk volume expansion. When spraying from CO₂, there is a range of parameters of state in which the formation of a two-phase vapour-liquid media during fluid expansion can be expected due to a relatively high critical temperature of CO₂. If that happens, then capillary effects lead to a partial collapse of the disperse structure. This problem is absent in case of spraying from supercritical nitrogen due to its low critical temperature, unreachable at RESS spraying. N₂ always gives higher bulk volume expansion of CNTs.

Effect of pressure and temperature on bulk volume expansion is defined primarily by the above-mentioned factor. When there is no risk of two-phase system formation during spraying, influence of pressure is trivial: higher fluid pressure gives higher bulk volume expansion.

According to SEM images, RESS-treatment leads to changes not only on macroscopic level, but also in CNT bundles microstructure. RESS-treated CNT samples are visually more laced, have more ragged texture and larger polydispersity. A certain shift of main CNT XRD signal towards larger 2θ values is observed for some RESS-treated CNT (from 24 to 30°). This XRD signal can be interpreted as analogous to {002} signal in graphite and can be attributed to an average inter-tube distance in CNT bundles. A shift to higher 2θ values can be interpreted as a decrease in the average inter-tube distance due to partial micropore collapse as well as to the decrease in CNT waviness.
Nitrogen porometry showed that dry RESS spraying give poorly reproducible quantitative results. Both unit surface area, total porosity and pore size distributions can vary substantially for the samples obtained in identical conditions. For instance, the discrepancies in unit surface area can be as high as several scores percentage points. It is unclear at the moment, whether this is a consequence of poor RESS reproducibility or of sample texture changes during sample preparation for the measurements.

According to photoluminescence data, direct injection into water allows obtaining higher level of CNT de-agglomeration than dry spraying with consecutive suspension in water. PL-maps of CNTs treated by direct RESS-injection into water contain clearly resolved peaks of individual tubes of different chirality. The degree of de-agglomeration is influenced by the type CNTs as well as by surfactant type and concentration.

The work is performed under the financial support of RFBR, project No. 18-29-06071.

Literature


Establishing patterns of the effect of physical-chemical and structural parameters of nanostructured sorbents being prepared on the quality of sorption of various contaminants from aquatic media is an important area of research regarding the development of efficient sorption materials.

In modern scientific literature, special attention is paid to the development of nanocomposites for liquid-phase sorption; in these composites, carbon nanostructured materials (carbon nanotubes (CNTs), and graphene in oxidized or reduced forms), forming the frame structure of such sorbents, act as carriers of functional substances. The use of these materials is due to the large values of the specific surface area and its almost complete accessibility to the molecules of the substance being extracted. Thus, the modification of such nanocarbon materials, for instance, with organic polymers contributes to an increase in their sorption capacity and the expansion of possible applications. Separately, it is possible to distinguish redoxites, a class of modifier material, which represent high-molecular-weight substances containing functional groups capable of reversible redox transformations (polyaniline, polypyrrole, chitosan, p-benzoquinone (p-BQ), cyclodextrin, polyethyleneimine, etc).

Quinoid materials (p-benzoquinone) capable of redox transformations are promising organic sorbents, but they do not possess developed porosity, specific surface area and sufficient stability in aquatic media. Considering this fact, synthesis of composite materials based on polyquinone-modified carbon nanostructures seems promising.

The authors of the present paper developed a technology for producing a promising sorption nanomaterial, polyhydroquinone/graphene oxide (PHQ/GO). The procedure is as follows. Initial components are loaded into a laboratory setup for nanocomposite synthesis, which consists of a round-bottom flask with two necks, aluminum container, heating element, thermometer, and overhead stirrer. With continuous stirring, the mixture components uniformly interact with each other under the
following synthesis conditions: water heating up to 95 °C, mixing speed 150 rpm, and argon consumption (to prevent substances from being destroyed by air components) 0.5 L/min. After 6 h, the suspension obtained after the synthesis is dispersed in a flow homogenizer and filtered with distilled water through a deashed filter. The filtration is completed when the orange color of the wastewater is absent. The material obtained after the filtration is placed in an airtight container.

It was important to identify the effect of the initial components/synthesis time quantitative ratio on the qualitative characteristics of the final product. The physical-chemical properties of the obtained nanocomposite were also determined using scanning electron microscopy, Raman spectroscopy, X-ray diffractometry, and thermogravimetry. Based on the characteristics obtained, a mechanism for the GO modification with PHQ was proposed.

It was established that the effective material synthesis duration is 6 h, since it allows to achieve the maximum degree of the GO saturation with the PHQ. At the same time, the graphene reaches its saturation with the PHQ using the p-BQ/GO initial component ratios of 1:10 and 1:12. Therefore, for further research, the ratio of 1:10 was chosen, for which the dry matter content in the material is 5 %, the PHQ content in the dry matter is 84.5 %, and the thermal stability of the synthesized nanocomposite is 180 °C.

The sorption properties of the obtained PHQ/GO nanocomposite prepared were studied regarding the removal of Cu$^{2+}$, Zn$^{2+}$ and Pb$^{2+}$ heavy metal ions from aqueous solutions. For quantitative analysis of the model pollutant contents in the aquatic medium, atomic absorption spectroscopy was implemented. The following adsorption capacity values were obtained: for Cu$^{2+}$ - 41.1 mg/g, for Zn$^{2+}$ - 25.2 mg/g, and for Pb$^{2+}$ - 63.3 mg/g.

Thus, the studies carried out prove the effectiveness of the proposed technology for the synthesis of the PHQ/GO nanocomposite for liquid-phase sorption processes.

The work was performed within the framework of the project part of State Assignment No. 16.1384.2017/PCh of the Ministry of Science and Higher Education of the Russian Federation.
Strict requirements to manufactured pharmaceutical products, including those from medicinal plant materials, require reliable technologies and accurate experimental data. In this regard, the study of the influence of various factors on obtaining biologically active substances requires special attention. One of the promising methods of extracting biologically active substances from medicinal plant materials is supercritical fluid extraction. The advantage of this method is the possibility of obtaining from a plant extracts of various consistencies by changing thermodynamic parameters of processing.

Our work presents the results of the pressure influence on the extraction process and the chemical composition received from *Satureja hortensis* extracts. In this purpose sequentially were obtained extracts by carbon dioxide from the same portion plant material under pressure of 10 and 30 MPa at constant temperature of 50°C [1]. The yield was 0.792 and 3.718% wt., respectively. For comparison, the essential oil was obtained with Clevenger apparatus by water vapor distillation (yield was 1.75 % wt.).

The component composition of the extracts was determined with the GC MS Shimadzu GCMSQP2010 plus. The results show that the qualitative and quantitative composition of the extract, obtained at pressure of 10 MPa and temperature of 50°C, is similar to the essential oil. The main components are α-Terpinene, p-Cymene, γ-Terpinene, Thymol, Carvacrol. The extract obtained at 30 MPa and 50°C, in addition...
to the substances named above, contained Linolenate-methyl, \( n \)-Hexadecanoic acid and others. The research shows that the increasing pressure of the extraction process at a constant temperature has positive effect not only on the quantitative output of the extract but also enriches its qualitative composition.

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Taking into account the enormous reserves of oil-saturated (bituminous) sandstones in the territory of the Russian Federation, in the context of increasing competition in the energy market, the authors of this work confirmed the possibility of introducing an innovative approach to oil production from oil-saturated (bituminous) sandstones and other rocks in the oil-bearing territories of the Republic of Tatarstan fluid (SCF) environments and the release of hydrocarbons and hydrophobic building materials.

SCF technologies based on the use of working media in sub- and supercritical fluid states are currently one of the most promising innovative scientific and technological areas, including oil production and refining.

Bituminous sandstone of the Spiridonovskoye field of the Republic of Tatarstan, which is a dark brownish to black sand, partially lumpy, is used as a raw material. Cemented lumps of two types - dark, larger (30–35%) and light gray lumps (7–8%). The bulk is represented by fine black sands. The content of petroleum products to 7.23 wt. %.

As the extractant used propane - butane mixture containing 75 wt. % propane and 25 wt. % butane. The critical parameters of propane and butane are characterized by the following values: propane: \( T_{cr} = 369.82 \text{ K} (96.67 \, ^\circ \text{C}) \), \( P_{cr} = 4.247 \text{ MPa} \); Butane \( T_{cr} = 425 \text{ K} (151.85 \, ^\circ \text{C}) \), \( P_{cr} = 3.797 \text{ MPa} \).

Figure 1 shows the release of hydrocarbons from tar sands in the process of extraction extraction using propane - butane extractant in a wide range of changes in operating parameters (P, T) of the process. As can be seen from the results, the technology allows to extract hydrocarbons up to 96.34 wt. %, and residual...
asphaltenes form a superstable hydrophobic film on the surface and pores of sandstones.

Table 1 presents the properties of the petroleum product obtained using the extraction process and the propane-butane extractant at a temperature 140 °C and a pressure 10 MPa.

![Fig. 1. The dependence of the release of hydrocarbons from tar sands from the pressure in the extraction process using propane - butane extractant at different temperatures: 1–80 °C, 2–100 °C, 3–140 °C; M2: M1 = 1.5: 1.][1]

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<td>20,90</td>
</tr>
</tbody>
</table>

Thus, a new environmentally safe and waste-free technology for the processing of oil-saturated sandstones using SCF extraction processes with a propane-butane extractant is proposed.

The research has been carried out with the financial support of Russian Science Foundation (project No. 18-19-00478).
The $\alpha$-GaPO$_4$ crystals are the most promising piezoelectric among the whole family of quartz-like materials. In addition to high piezoelectric characteristics, they have a unique (up to 933 °C) temperature stability of the quartz-like structure. Typically, $\alpha$-GaPO$_4$ crystals are grown from concentrated (6 - 15 M) solutions of orthophosphoric and sulfuric acids or their mixtures by the method of gradual temperature increase from 150 to 260 °C or by the flux method by slow cooling from 950 to 600 °C.

In this work the growth of $\alpha$-GaPO$_4$ crystals was carried out by the evaporating-recirculation method developed by us earlier, successfully used for growing $\alpha$-GeO$_2$ crystals. Since $\alpha$-GaPO$_4$, in contrast to metastable germanium oxide, is in the stability region of the quartz-like (trigonal) structure up to 933 °C, it was possible to raise the crystal growth temperature to 260 °C. The experiments were carried out in special crystallizers made of 1X18H9T stainless steel lined with fluoroplastic (PTFE). The growth of $\alpha$-GaPO$_4$ crystals was carried out epitaxially on quartz substrates, using fine-crystalline $\alpha$-GaPO$_4$ as a charge. The retrograde nature of $\alpha$-GaPO$_4$ solubility in solutions of concentrated phosphoric and sulfuric acids below the temperature of 335 °C creates the danger of seed dissolution even when preparing the crystallizer for the experiment. In this regard, the use of quartz substrates for the epitaxial growth of $\alpha$-GaPO$_4$ crystals is of particular importance, since quartz is practically insoluble in solutions of phosphoric and sulfuric acids. Crystallization was performed on substrates of different crystallographic orientations, cut from synthetic quartz. The quartz substrates were located in the lower, hotter growth chamber. A perforated basket with a charge — small (up to 3–5 mm in diameter) fragments of $\alpha$-GaPO$_4$ was placed above this camera. In the central part of the charge basket has a hole for the passage of steam from the lower growth chamber to the refrigerator, located directly above the charge. The cooler directing devices for condensate drain are arranged in
such a way that a large proportion of condensate flows directly into the charge chamber and dissolves the charge material. The walls of the bottom part of the charge chamber have holes with a diameter of 1–1.5 mm for condensate drain with a partially dissolved charge into the initial solution, into the growth chamber with seeds suspended in it. As a result, supersaturating occurs in it, leading to the nucleation and growth of α-GaPO₄ crystals. The process takes place until complete exhaustion of the charge. The growth rates of α-GaPO₄ crystals on the seed reach 1.0 mm/day under certain conditions. Despite the relatively low temperatures and pressures, crystals grown in solutions of sulfuric acid do not contain molecular water, and the hydroxyl group OH, although present, but in very limited quantities.

![Epitaxial growth of α-GaPO₄ crystals on quartz substrates ZY orientation](image)

Thus, the α-GaPO₄ single crystals were grown on a quartz substrate using the evaporation-recirculation method for the first time. Crystal growth was carried out in aqueous solutions of mixtures of hydrochloric, phosphoric or sulfuric acids at temperatures of 150–260 °C and pressures of 3–5 MPa. Crystal growth rates reach 1.0 mm/day. Despite the relatively low temperatures and pressures the crystals do not contain molecular water, and the hydroxyl OH group is present in very limited quantities.

The reported study was funded by RFBR, project number 17-05-00976.
SOLVATION OF ETHANOL, PHENOL AND GUAYACOL IN NORMAL AND SUPERCRITICAL CONDITIONS

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Lignin is an irregular natural polymer whose monomers are phenol derivatives: guaiacyl, syringyl, hydroxyphenol - linked by β-ether, biphenyl, and heterocyclic bonds. Ligno-containing materials are the most common natural material with a practically inexhaustible resource: every year the plant world produces about 170 million tons of lignocellulose [1]. Due to the availability and abundance of functional groups, natural lignin can be used as a raw material for the production of various chemical substances: phenols, alcohols, esters, acids, hydrocarbons, as well as new composite materials. However, the high chemical resistance of lignin does not allow full use of the potential of this raw material and currently only 2% of all technical lignin is used [2]. The development of lignin processing techniques is hampered by the irregular structure and complex variable composition of the natural polymer, which depends on the type of raw material (wood grade, type of agricultural crop, etc.). One of the promising ways of processing natural lignin is its depolymerization under supercritical conditions, however, it is difficult to identify patterns of chemical transformation of lignin due to the irregular structure of the natural polymer and the strong dependence of the reaction products on the type of raw material used [3]. In this connection, the role of the computer molecular dynamics experiment increases, which makes it possible at the molecular level to see the structural and dynamic features of the reaction medium depending on the chemical nature of the components.

At the starting level, in order to determine the role of various functional groups in the processes of chemical transformation of lignin in aqueous solutions under supercritical conditions, it seems necessary to study the behavior of aqueous solutions of small molecules containing functional fragments of natural lignin under normal and supercritical conditions: benzene rings and – OH, – Me and – OMe groups.

In this paper, we investigated aqueous solutions of alcohols of different nature: ethanol (1), phenol (2) and guayacol (3) under normal and supercritical conditions.
Our attention was focused on the study of the dynamic properties of solutions and the features of the solvation of various functional groups in different molecules.

In the framework of the task, classical molecular-dynamic modeling of the structure of aqueous solutions containing 2 mass. % alcohol (ethanol, phenol and guvayacol) - in normal (T = 298 K, p = 1 atm.) and supercritical conditions (T = 673 K, p = 230 atm.) in the NVT ensemble. The computational cell contained 10,000 molecules. In the simulation, the software package GROMACS [4], the potential of OPLS-AA [5] for alcohols and TIP4P for water were used. The analysis of the behavior of the computational systems was carried out on trajectories with a length of 10 ns. The radial distribution functions (RDF) for the distances between the oxygen atoms of the water and alcohol molecules, self-diffusion coefficients, and dielectric constant are calculated. The analysis of the solvation of molecules through the formation of hydrogen bonds between the functional groups of alcohol molecules and the oxygen atom of water molecules is carried out. The revealed structural features of the solutions under supercritical conditions are compared with the data for pure water.

*The Russian Foundation for Basic Research supported this work, grant 18-29-06072.*

THE COMPOSITION OF EXTRACTS OF PINUS SILVESTRIS WOOD GREENERY OF SUBARCTIC TERRITORIES OF THE EUROPEAN NORTH OF THE RUSSIAN FEDERATION

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The comparative analysis of methods of extractives extraction from wood greenery of Pinus Silvestris is carried out. The efficiency of the method of supercritical fluid extraction by binary solvent (SC CO\textsubscript{2} with ethanol) is promising for the increasing of the yield and the spectrum of extractives.

A large number of works are devoted to the study of the chemical composition of coniferous trees, and it is shown that it is characterized by the presence of components that differ in their chemical nature and properties (resin and fatty acids, aliphatic and aromatic hydrocarbons, phenols, terpenes, etc.) [1]. When choosing an extractant, we should take into account that it must extract the largest possible amount of extractives (ES). Ethanol is most common extractant used for wood greenery; it extracts chlorophyll, carotenoids, vitamins, tannins. Traditional methods of components extraction from wood greenery are the method of infusion with ethanol, as well as hydro distillation. Supercritical fluid extraction (SCE) by carbon dioxide is a promising method of ES extraction [2]. Scots pine is one of the tree species that has an ancient tradition of use in medicine, its wood greenery are rich in vitamins, and its phytoncidic activity is superior to many types of tree species [3].

The aim of the work was to evaluate the effectiveness of using the supercritical fluid extraction method for extraction of the complex of extractive substances of Scots pine wood greenery.

Infusion with ethanol was carried out in static mode at 45-50°C, and hydro distillation - in the Clovenger apparatus. SCE of wood greenery by supercritical CO\textsubscript{2} and ethanol as co-solvent was carried out at 45 °C and 150 MPa for 1 hour; CO\textsubscript{2}
flowrate - 20 g/min, co-solvent flowrate - 2 g/min. The volatile ES were determined by gas chromatomass-spectrometer GS-MS QP-2010Ultra (column Rtx-5MS); about 90 % of the compounds were identified with confidence level above 85 % (table.1).

Table 1 - Group composition of the investigated extracts

<table>
<thead>
<tr>
<th></th>
<th>Hydro distillation</th>
<th>Infusion with ethanol</th>
<th>SCE with CO₂</th>
<th>SCE with CO₂+ethanol</th>
</tr>
</thead>
<tbody>
<tr>
<td>The yield of extractives, % (abs.)</td>
<td>2,4 %</td>
<td>10,3 %</td>
<td>4,3 %</td>
<td>8,5 %</td>
</tr>
<tr>
<td>number of components / contents, % (rel.) of total sum of components</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Monoterpenes</td>
<td>8 / 22,15</td>
<td>2 / 0,7</td>
<td>3 / 0,85</td>
<td>1 / 0,28</td>
</tr>
<tr>
<td>Sesquiterpenes</td>
<td>9 / 22,11</td>
<td>4 / 3,8</td>
<td>4 / 4,68</td>
<td>4 / 5,56</td>
</tr>
<tr>
<td>Diterpenes</td>
<td>1 / 34,69</td>
<td>1 / 39,9</td>
<td>1 / 61,12</td>
<td>1 / 49,55</td>
</tr>
<tr>
<td>Oxygen-containing derivatives of terpenes</td>
<td>4 / 18,58</td>
<td>3 / 5,79</td>
<td>6 / 14,44</td>
<td>4 / 8,46</td>
</tr>
<tr>
<td>Monobasic carboxylic acids</td>
<td>0 / 0</td>
<td>1 / 1,43</td>
<td>1 / 0,86</td>
<td>1 / 1,35</td>
</tr>
<tr>
<td>Saturated fatty acid</td>
<td>0 / 0</td>
<td>1 / 1,47</td>
<td>1 / 1,35</td>
<td>1 / 1,5</td>
</tr>
<tr>
<td>Alkanes</td>
<td>0 / 0</td>
<td>1 / 19,57</td>
<td>0 / 0</td>
<td>1 / 5,92</td>
</tr>
<tr>
<td>Sugars</td>
<td>0 / 0</td>
<td>1 / 14,92</td>
<td>1 / 1,13</td>
<td>1 / 3,74</td>
</tr>
</tbody>
</table>

According to the obtained data, the main part of components extracted by the method of hydro distillation consists of mono- and sesquiterpenes. The method of infusion with ethanol allows expanding the list of extracted compounds (acids, alkanes, sugars). Supercritical fluid extraction with CO₂ predominantly allows the extraction of diterpene 13(16),14-labdien-8-ol (50-60% of the total amount of the substances). The obtained extract can be used for the synthesis of aromatic substances, as well as in pharmacology. The increasing the efficiency of the method is achieved by using a binary solvent, one of the components of which is ethanol, which has an affinity for the extracted components. This increases the yield and expands the range of individual compounds.

This research was funded from FASO of Russia (project № AAAA-A18-118012390231-9) and Ural Branch of RAS (project № AAAA-A18-118012390228-9). The research was performed using the instrumentation of the Core Facility Center "Arktika" (NArFU) and Core Facility Center “KT RF in the field of environmental safety of the Arctic” (FCIARctic).
REFERENCES


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SUPERCRITICAL FLUID EXTRACTION OF USNIC ACID FROM THE LICHEM USNEA SUBFLORIDANA

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Lichens of the genus Usnea are characterized by the presence of specific lichen acids such as usnic, barbate, fumarprotocetraric and squamatic. Usnic acid (UA) is the main secondary metabolite for these lichens. UA [2,6-diacetyl-7,9-dihydroxy-8,9b-dimethyl dibenzofuran-1,3 (2H, 9bH) dione] is one of the most studied and common metabolites of lichens with a wide range of antimicrobial, antiviral and anti-inflammatory properties [1].

Classical methods for the isolation of biologically active compounds from the plant raw materials are extraction methods using organic solvents. These include maceration (infusion), percolation (continuous filtration of the extractant through the layer of the raw materials), repercolation. The advantage of these methods is the ease of execution and equipment. The disadvantages include the duration of the extraction process, the high content of impurities in the extracts. Along with the above-mentioned traditional methods of extraction, the modern methods of extraction, such as supercritical fluid extraction (SCFE) and accelerated solvent extraction (ASE) are currently used. These methods can significantly increase the yield and improve the quality of the target product including the isolation of UA from lichens [2,3].

Thus, the purpose of this work was to optimize the conditions of supercritical fluid extraction of the UA from the lichen Usnea subfloridana. The main optimized parameters were the extract yield (W,%), the UA content in the extract (A,%) and the yield of the UK from absolutely dry raw materials (B,%). Supercritical fluid extraction was performed on an MV-10ASFE unit (Waters, USA).
For the mathematical description of the process of supercritical fluid extraction of the UA from *Usnea subfloridana* and determining the optimal parameters of the process the planned experiment was carried out and a central composite uniform plan design of the second order was applied. When constructing the plan, the main pressure level (X), the test temperature (Y) and the process duration (Z) were chosen respectively the following parameters: 250 atm, 600 °C and 55 min. The intervals of variation were 60 atm, 150 °C and 15 min. The star shoulder (α) is 1.682.

As a result of the mathematical processing of experimental data using MS Excel, еру regression equations (1-3) were obtained that adequately describe the extraction process. The value of the Fisher criterion does not exceed the threshold values, the multiple correlation coefficients are in the range of 0.75-0.95 with an average relative error of approximation of experimental data of 5.0 - 17.0%.

\[
W = 0.56 - 0.086x - 0.024y - 0.035z + 0.047y^2 + 0.127z^2 \quad (1)
\]

\[
A = 36.66 + 1.213x + 2.259y + 3.626z - 5.294xy - 2.51x^2 - 1.988y^2 \quad (2)
\]

\[
B = 0.75 + 0.035x + 0.048y + 0.047z - 0.084xy + 0.029xz - 0.093x^2 - 0.051y^2 \quad (3)
\]

where \( x = (X - 250)/60; \ y = (Y - 60)/15; \ z = (Z - 55)/15 \)

Thus, the optimal parameters of the process of the UK extracting from the lichen of *Usnea subfloridana* by the method of supercritical fluid extraction using supercritical carbon dioxide as a solvent in the given range of factors were determined by the method of an active planned experiment. According to the used model, the optimum process conditions were proposed: duration of 80 min, a temperature of 600 ° C and a pressure of 150 atm. According to the used mathematical model, the predicted yield of the extract is 1.01 %, with the content of the UA of 33.7% and the output of the UA from the lichen 0.43%. When conducting a confirmatory experiment, the values of W, A, and B were 0.98, 35.2, and 0.49, respectively, which indicates the adequacy of the applied model.

**References**


NEW ENVIRONMENTALLY-CLEAN “ONE-POT” METHOD FOR OBTAINING PENTANTHER ALKALOIDS IN THE MEDIUM OF SUBCRITICAL WATER: ISOMERIZATION OF PLANT ALKALOID BOLDIN IN HIS PENANTRANE ANALOGUE

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The purpose of this work was the development and study of a new low-cost and environmentally friendly method of one-step ("one-pot") method for the modification of isoquinoline alkaloids in subcritical water (SCR) with the aim of obtaining their phenanthrene structural analogues. The plant aporphin alkaloid boldin was studied as a model compound. It has been demonstrated that, in a subcritical water environment, the aporphine alkaloid boldin is isomerized into its phenanthrene isomer, the alkaloid secoboldin II.

It is shown that changing only one process parameter (SCR temperature) allows changing the composition of products obtained using the new technology (“one-pot”). The procedure developed for the production of secoboldin in SCR requires only one stage, unlike the traditional multi-step procedure, which uses expensive and toxic organic solvents.
The proposed procedure has the potential for the future development of fast and inexpensive technologies for the production of phenanthrene alkaloids and their derivatives from aporphine alkaloids for the pharmaceutical, food and cosmetic industries.

Acknowledgments
The work was done with the financial support of the internal grant of the Southern Federal University (Project No. VNGr-07 / 2017-04)
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**THERMO PHYSICAL PROPERTIES HIGH H-ALKANES DISSOLVED THEREIN SCF MEDIUM**

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On the background of substantial depletion of petroleum deposits of low and medium density and viscosity rises sharply in the world problem of increasing the volume of oil production by engaging in the development of high-viscosity oils [1]. The share of heavy and high-viscosity oil in the world oil production has reached 25%. In the Volga-Ural oil province is concentrated to a quarter of Russian reserves of heavy and high-viscosity oil. Most of them - up to 80% is located in the territory of the Republic of Tatarstan (RT). One of the obstacles encountered in the extraction of heavy oil when pumping it through pipelines is viscosity. Kinematic viscosity of the oil, especially in winter often comes up to 1000 mm$^2$/s, which makes it virtually impossible pumping. by pipeline its kinematic viscosity should be less than 150 mm$^2$/s for oil transport. RT Oil companies to be able to pump oil through pipes from wellhead to the primary treatment in winter simultaneously use two ways to reduce the viscosity of the plant. The oil is introduced additive "Kompliteks" reduces viscosity up to three times, and further heated oil boiler plant. At the boiler plant installed on the track pumping station. From considerations eliminate cavitation effect to the pump station is removed from the oil dissolved therein associated gas. Pumping pressure 2.5-2.6 MPa is set, although the equipment allows to maintain the pressure of 5-6 MPa. So, at a cost of 1 ton of additives in 1 mln. Rub. and the length of 17 km of the pipeline cost of oil increases to 50% in the winter! It is known [1], that the kinematic viscosity average heavy oil Volga-Ural oil province at reservoir conditions (P and T) at a depth of 1000-2000 m is about 125 mm$^2$/s. Such suitable for pumping oil viscosity due not only to high temperature in the reservoir (40-60°C), but mostly dissolved in the oil associated petroleum gas. Thus calculated by REFPROP application [2], the values of the critical parameters (T$\text{cr}$ = 205.01 K; P$\text{cr}$ = 6.0425 MPa) for the associated gas with the composition given in weight parts: methane -
0.82672; ethane - 0.07737; nitrogen - 0.049807; propane - 0.020751; CO₂ - 0.011696; isobutane - 0.003426; n-Butane - 0.005163 et al indicate that at reservoir conditions, this gas may be in a supercritical fluid state. When the depth of oil and more than 1000 m.

When driving oil pipeline and borehole temperature and pressure are reduced, which leads to the separation of oil dissolved associated gas, oil viscosity increase and solidification of the parafins (alkanes Macromolecular). The wellhead and the inner surface of tubes are accumulated asphalt-waxy deposits impeding the passage of oil. Investigation of the influence of dissolved gas in the associated heat physical and transport properties of high-viscosity oil and its individual components is an important concern in improving the volume of production is difficult to extract oil.

One of the promising methods of complex measurement of heat and thermal diffusivity, thermal activity and viscosity of gases, liquids, substances in the solid state and their solutions including, in the critical region and the state is the method of pulse-heated low-inertia probe [3, 4].

As part of this work were obtained experimental values of thermal conductivity of n-tetracosane - Representative n-alkanes and mixtures of n-alkanes (paraffin wax) of C₁₈H₃₈ (n-octadecane) to C₃₅H₇₂ (pentatriokontan). In the transition from solid to liquid is observed in races values of thermal conductivity. Thus, the thermal conductivity of n-tetracosane abruptly decreases from 0.41 W/mK to 0.153 W/mK when the temperature changes from 323.48 K to 323.73 K. In the case of the formula - paraffin is a smooth change in thermal conductivity at when the phase transition temperature varies from 318.08 K to 325.0 K.

The work was supported by the Ministry of Education of the Russian Federation in the framework goszadaniya 13.5112.2017 / 8.9 and RNF agreement 18-19-00478.

In achieving the optimal combination of the properties of a catalyst, both the ensuring of the desired composition of catalytic material (chemical, phase) and its fine “tuning”, i.e. particle sizes of the components, their relative position and morphological features of the system at different levels (from atomic to macroscopic), are the key factors.

For example, high structural sensitivity, which is a dependence of the catalytic properties on the phase composition and morphological features of the components of the catalyst which in its turn governed by the preparation technique, is a characteristic of the mixed oxide systems used as promising catalysts for the oxidative coupling of methane. Such systems should not have a high specific surface, but they should have a certain chemical and phase composition, as well as an optimal morphology. To achieve a combination of these characteristics at thermal synthesis is difficult because of the uncontrolled interaction between the carrier and the applied components.

Treatment of catalyst precursors at relatively mild conditions: in an aqueous fluid medium at temperatures below and above the critical point of water gives unique opportunity to direct the transformation of the deposited active phase precursor towards the formation of the target compound without involving the support material into this chemical transformation as well as to manage the structure of the supported compound.

One of the features of the experiment in aqueous fluid is the complex mass transfer. For a number of reasons many processes under conditions of sub- and supercritical water treatment are often carried out in batch reactors. This implies a low-temperature step when some raw materials, reagents, and liquid water are loaded into
the reactor possibly followed by creating an additional atmosphere (inert or, on the contrary, reactionary) and subsequent heating to temperatures at which the chemical process is expected.

In this case, temperature gradients may occur in the reactor. When the condition parameters of phase transformations are reached, the presence of a temperature gradient can lead to the appearance of liquid water in those zones of the reaction volume where it was not anticipated when planning the experiment. Depending on the nature of the object under study and on which stage of the process a liquid is formed, it can cause disturbance of the planned course of experience. As a result, uncontrollable distortions of the experimental data may take place or the appeared effects, explanation of which without taking into account the dynamics of the appearance/disappearance of the liquid phase and the characteristics of its transfer in the system, can distort the actual picture of the process.

As an example, the synthesis of certain oxide compounds or phases by treatment of solid precursors in aqueous fluid can be considered. The treatment can be carried out either by liquid water or steam below the critical point, or by supercritical water of different density. Therefore, the kinetics of the process and the properties of the synthesized product can strongly depend on the phase state of the water during processing.

In this work, we considered a case in which a solid sample is treated by subcritical steam or supercritical (SC) water, i.e. the contact of the sample with the liquid water phase should be excluded.

A model experiment was carried out in a 100 ml SK-500 autoclave (SCHAG, Russia) operating under the second scheme, i.e. when only the side wall are heated by a furnace. A solid sample of $\alpha$-Al$_2$O$_3$ was placed in an additional inner container located in the middle of the reactor on a special stand; water was added into the outer volume of
the autoclave. Then the autoclave was heated to 300°C. After cooling the system, a significant amount of water was found in the container and the solid sample was completely immersed in it. It is likely that due to the temperature difference between the heated wall and the relatively cold cover conditions for water condensation on the autoclave cover were created.

In the absence of the container with a sample in the autoclave, a continuous cyclic process of evaporation-condensation of water would take place: re-condensation of water, i.e. a liquid phase formation, happens on the cold horizontal surface of the cover followed by the drop detachment or its runoff, for example, down the well for a thermocouple. In the presence of the sample container liquid water dropped the inside it. Thus, the sample was treated not by steam or SC phase, but by liquid water.

In the described case, a relatively simple solution of the problem can be proposed, namely, to use a leaky inner container with a lid that prevents steam condensate formed on the elements of the autoclave to get inside the container with the sample. A scheme of such a container is shown in Fig. 1. Experiments using this construction showed that, in this case, the sample is protected from the contact with liquid water, i.e. at a temperature below the critical point of water, hydrotreatment of the sample takes place, as it was planned in the experiment.

*This work was financially supported by RFFI (project No. 18-29-06055 mk).*
Creating environmentally friendly biomaterials with useful properties is one of the key tasks of modern science. The urgency and the need to develop such materials are due to the existing high demand for polymeric materials for various fields of activity, primarily biomedicine. Modern biomedical materials have a number of stringent requirements for their safety, such as non-toxicity, biocompatibility and biodegradability. Organic aerogels based on natural polysaccharides, as a rule, have all of the above properties, moreover, unlike inorganic aerogels, they are less friable and less fragile, they do not collapse to a powdery state during deformation. Due to the large specific surface area, high porosity and ability to control the structure, polysaccharide aerogels have a high potential for use as carriers of medicinal substances. In addition, by changing the nature of the polymers from which the structural matrix of the aerogel is made, by adding different functional groups, it is possible to change the selectivity of the aerogel to adsorb various substances. Thus, the purpose of this work is the directed synthesis of aerogel materials based on the sodium alginate – chitosan interpolyelectrolyte complex (IPEC ALNa-CT) and to study the possibility of using the resulting aerogels as carriers for drug delivery. For the creation of aerogel materials, natural ionic polysaccharides ALNa and CT are chosen as precursors in this work. The choice is due to the fact that they do not exhibit toxic side effects when in contact with a living organism, are biocompatible and have their own physiological activity. Due to the presence of oppositely charged ionic groups ALNa and CT, they interpolyelectrolyte react, which eliminates the use
of cross-linking agents and ensures complete biodegradability and safety for humans [1,2].

As a result of the research conducted, the features of the formation of mesoporous organic aerogel materials based on the sodium alginate – chitosan interpolymer complex were studied. The aerogel obtained on the basis of IPEC ALNa – CT is a highly porous white fibrous material that retains the morphology of the original IPEC. As a result of drying, a slight aerogel shrinkage is observed. The maximum specific surface area of aerogels was 260 m$^2$ g$^{-1}$ and the average pore size was 16 nm. The possibility of using the obtained aerogel to create wound dressings with the inclusion of a synthetic medicinal substance (antibiotic levomycetin) was shown. Slow release of the drug substance (70% within 5 hours) from the aerogel matrix provides a prolonged and safe delivery of the drug to the wound surface.

This research was funded from the project agreement № AAAA-A18-118012390231-9 “Physico-chemical, genetic and morphological bases of the plant objects adaptation under the conditions of the changing climate of high latitudes” We used the equipment CCU SE “Arctic” (Northern (Arctic) Federal University) and the equipment of CCU SE CT RF-Arctic (N. Laverov Federal Center for Integrated Arctic Research).

References


SUPERCRITICAL FLUID EXTRACTION OF TURPENTINE OIL OF FENNEL (PEUCEDANUM GRAVEOLENS) SEEDS

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Oil of fennel seeds finds various and broad application in traditional medicine, being the important instrument of regulation of water balance of an organism. Essential oils of fennel seeds enhance motility of a digestive tract and stabilize a metabolism in an organism. The principal active components of fennel oil are terpenes such as carvone and a limonene and also dihydrocarvone [1]. Supercritical fluid extraction (SCFE) of terpenes of oil fennel by carbon dioxide can be a hydrodistillation alternative [2]. The purpose of work was studying of a possibility of terpenes from fennel seeds SCFE and definition of its optimal parameters.

Table. Influence of extraction conditions on an exit of extract and maintenance of an essential oil.

<table>
<thead>
<tr>
<th>T, °C</th>
<th>P, at</th>
<th>Yield of extract, %</th>
<th>Maintenance of an essential oil, %</th>
<th>Oil extraction extent, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrodistillation</td>
<td>4,3</td>
<td>100</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>80</td>
<td>1,2</td>
<td>98,9</td>
<td>28</td>
</tr>
<tr>
<td>30</td>
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Seeds of garden fennel (Peucedanum graveolens) which is grown up in Primorsky district of the Arkhangelsk region were chosen as the object of a research. The humidity was 8%, fraction 2.0 – 0.2 mm makes of 80% of the ground exemplar, the maintenance of an essential oil was 4.3%. The essential oil contained 53% of D–limonene and 41% of a carvone, also α–phellandren, dihydrocarvone, dill esther, β – myrcene, dihydrocarveol and carveol were presented.
SCFE was carried out with use of the MV-10ASFE installation (Waters, the USA) [3].
The maintenance of an essential oil in the seeds of fennel and extracts received by the SCFE method was determined by the Klevendzher’s method.
Results of a research of fluid temperature and pressure effects upon an yield of extract and contents an essential oil in it during 40 minutes of extraction process are given in the table.
Influence of duration of extraction on oil extraction extent is investigated with a pressure of 150 at and temperature of 40 °C. The optimum duration of process was 30 minutes.

Conclusions:
1. Supercritical fluid extraction by carbon dioxide allows to take from 30 to 100% of terpenes, contained in Peucedanum graveolens fennel.
2. Optimal parameters of extraction are pressure of 150 at, temperature of 40 °C, duration of 30 minutes, liquid module 5,4.

This work was carried out using the equipment of CCU RO Arktika NArFU with assistance of the Russian Fundation for Basic Reseach (grant No. 18-44-292002 p_mk).

LIST OF REFERENCES
Modern coherence-domain techniques of random media diagnostics are based on the statistical analysis of coherent light multiple scattered by a probed medium. The estimation of the statistical parameters of stochastic distributions of light intensity occurring due to multiple scattering (such as the oscillation index, or the contrast, or the structure function, or the correlation function, etc.) gives the possibility to characterize the structural features of examined media and the processes inside the medium.

The diffusing-wave spectroscopy based on the analysis of the spectral or correlation characteristics of fluctuating light field provides an adequate information about the relaxation of two-phase systems in the course of transition between equilibrium thermodynamic states\(^1\). Use of a specially designed software in the dynamic light scattering techniques allowed for the estimations of the diffusion coefficient of particles in liquids, recovery of the particle size distributions, and other parameters of multi-phase systems\(^2,3\). The efficient technique for study of the non-stationary mass transfer in mesoporous systems is based on the correlation analysis of spatial-temporal fluctuations of scattered laser light. The fundamental features occurring in the course of formation of the ensembles of liquid-crystal (LC) domains in LC-polymer composites under UV-cured polymerization of LC-monomer mixtures were established using the full-field speckle correlometry based on analysis of the structure functions of speckle-modulated light fields\(^4\).

In this work we consider the algorithm of analysis of the statistical and correlation parameters of radiation scattered by a dispersed structured medium with the time-dependent optical properties. Porous structures synthesized using supercritical fluidic technologies can be considered as such time-varying media, in whose the structure-
forming elements change their sizes and shapes. These changes manifest themselves in the varying optical transport parameters and reflectometric properties of the medium.

Acknowledgements: The reported study was funded by RFBR according to the research project № 18-32-00584 (relating development of the data processing algorithms) and by RFBR according to the research project № 18-29-06024 (relating sample preparation and conducting an experiment).


MULTIPHASE STRUCTURED SYSTEMS

Multiphase structured systems are used in various areas of modern industry and biomedicine. Porous polymer structures are widely applied as the functional membranes providing a necessary penetrability of liquid or gaseous components [1-2], or as the three-dimensional matrices in tissue engineering [3].

Optical properties of porous multiphase systems are defined by their structural parameters: the porosity, the variance of the pore size distribution, and the pore shapes. Analysis of laser radiation scattered by a multiphase system allows for obtaining the information about the functional and structural properties (such as the concentration and shape of the inhomogeneities, features of the structure organization and evolution) of the probed object.

The method of laser full-field speckle correlometry gives the possibility for the analysis of the kinetics of the dispersive system evolution at the spatial scale of the order of the wavelength of probe light. For example, the correlation time of intensity fluctuations in the detected optical signal is the informative parameter in the case of characterization of structural changes in two-phase systems under the varying temperature [4].

In this work, we present the results of analysis of statistical and correlation properties of stochastic interference patterns occurring due to scattering of the laser light by the model foamed media with the varying optical properties. The samples of Gillette
Foam regular were used as the model of two-phase system with the varying optical and structural properties in the course of aging. The results of analysis of the trend in behavior of the correlation time of intensity fluctuations at large time scales in the course of transition from the “wet” to “dry” state are presented. In addition, the influence of liquid component evaporation and its drainage through the Plateau channels on the statistical and correlation parameters of intensity fluctuations in the scattered laser radiation is considered.

This problem seems relevant from the viewpoint of development of the physical basis for novel approaches in the coherence-domain reflectometry in application to the diagnostics of porous structures and dynamics of the structural instabilities in the course of evolution of foamed substances obtained using supercritical fluidic technologies.

Acknowledgements: The reported study was funded by RFBR according to the research project № 18-32-00584 (relating development of the data processing algorithms) and by RFBR according to the research project № 18-29-06024 (relating sample preparation and conducting an experiment).


ALDOL CONDENSATION OF SUPERCRITICAL ACETONE ON HETEROGENEOUS CATALYSTS

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Acetone is used not only as a solvent but also as a source for the synthesis of other industrially important solvents: diacetone alcohol, mesityl oxide, methyl isobutyl ketone and isophorone. Their preparation includes the stage of aldol condensation of acetone. In industry solutions of alkalis and mineral acids are used as catalysts. The heterogeneous catalysts for the aldol condensation of acetone described in the literature are characterized by low stability (the reaction was carried out in the gas phase), associated with surface coking and blocking of active sites. The purpose of this work was to study the aldol condensation of acetone in the supercritical state.

In this study calcium and magnesium stannates (CaSnO₃ and MgSnO₃) were used as catalysts. Synthesized catalysts were characterized by XRD, \( S_{\text{BET}} \), IR, SEM / TEM. Acetone condensation was carried out in the temperature range of 250-400 °C and pressures of 20-125 atm. The reaction products were analyzed by gas chromatography and chromatography-mass spectrometry.

The major products under studied conditions were mesityl oxide and isophorone. The MgSnO₃ catalyst was more active than CaSnO₃. So, the conversion of acetone on MgSnO₃ exceeded 25% with selectivity towards mesityl oxides of more than 80% at 250 °C and 75 atm. A close conversion of acetone on CaSnO₃ was achieved only at 375 °C. It was shown that the supercritical media favorably affects the activity and stability of these catalysts in acetone self-condensation.
INFLUENCE OF THE VARIOUS PARAMETERS ON THE RETENTION OF ANALYTES ON POLAR STATIONARY PHASES UNDER CONDITIONS OF SUPERCritical FLUID CHROMATOGRAPHY

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The aim of this study is to investigate the effect of various parameters (temperature, back-pressure, modifier amount, type and concentration of additive) on the characteristics of «stationary phase CO₂-MeOH» system using linear solvation energy relationship (LSER) methodology, which is based on the following equation:

\[
\log k = c + eE + sS + aA + bB + vV + d^-D^- + d^+D^+
\]

In this equation, capital letters represent the solute descriptors, related to particular interaction properties; c is the model intercept term and is dominated by the phase ratio; E is the excess molar refraction and models polarizability contributions from \( n \) and \( \pi \) electrons; S is the solute dipolarity/polarizability; A and B are the solute overall hydrogen-bond acidity and basicity; V is the McGowan characteristic volume in units of cm\(^3\)•mol\(^{-1}\)/100; \( D^- \) represents the negative charge carried by anionic and zwitterionic species, and \( D^+ \) represents the positive charge carried by cationic and zwitterionic species. The system constants \( (e, s, a, b, v, d^-, d^+) \), obtained through a multilinear regression of the retention data for a certain number of solutes with known descriptors.

During the work, a number of polar sorbents were used, which are widely used in SFC: bare silica UPC² BEH, cyanopropyl phase HSS Cyano, ethylpyridinium phase UPC² BEH 2-EP and zwitterionic sorbent Nucleodur HILIC. For a given stationary phases, retention of 89 analytes of different classes was investigated at various conditions and LSER-coefficients were calculated.
It has been established that neither pressure nor temperature affect the selectivity in the case of selected stationary phases. On the other hand, the effect of these parameters on the retention in the general case is complexly predictable and depends on the type of sorbent. Pressure rising leads to a weak increase of hydrogen bonded interactions, except for the cyanopropyl phase. Thus, pressure has a greater effect on analytes incapable of such kind of interactions.

Temperature rising leads to an intensification of orientational and induced van der Waals interactions; thus, the greatest effect is observed for stationary phases capable of such interactions as cyanopropyl sorbent.

As expected, increasing of the co-solvent amount in the mobile phase leads to a retention decrease of all analytes due to the growth of the eluting force. Accordingly, for the selected stationary phases, a decrease of all LSER-coefficients is observed, most pronounced for $a$ and $b$, reflecting the intensity of hydrogen bonded interactions.

It was found out that the introduction of additives primarily affects the parameters associated with ionic interactions. When trifluoroacetic acid is added, the coefficient $d^-$ becomes negative, and the coefficient $d^+$, on the contrary, increases substantially, indicating a decrease in the retention of compounds in the anionic form, for example, acids. Introduction of diethylamine and ammonium acetate leads to an increasing of the coefficient $d^-$, while the coefficient $d^+$ remains practically unchanged.

Introduction of the water leads to complex changes in the retention mechanism, affecting not only the coefficients $d^+$ and $d^-$ but also the coefficients associated with interactions due to hydrogen bonds ($a$, $b$).

*Research work was carried out in the framework of the state order of the Ministry of Education and Science of the Russian Federation in the field of scientific activity № 4.3273.2017/ПЧ. The work was performed in the Arktika Core Facility Center of the Northern (Arctic) Federal University under support of the Ministry of Education and Science of the Russian Federation.*
PREPARATION OF ULTRADISPERSE SYSTEMS DURING EXTRACTION OF SUB-CRITICAL WATER FROM MILK THISTLE SEEDS

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Biologically active compounds (BAC) of milk thistle seeds (*Silybum marianum* L.), such as silybin, silikristin, silydianin, have hepatoprotective properties, but they are poorly soluble in water, therefore, have limited bioavailability for our organism. One of the methods to overcome the low solubility and permeability of the BAC through biological membranes is to obtaining extracts using subcritical water, resulting in the formation of micro- and nanoemulsions.

The aim of the work is to study the process of formation of ultradisperse systems during the extraction of BAC from the milk thistle seeds using subcritical water, the study of their stability. It was established that the subcritical extract of milk thistle is stable only for a day, and thereafter there is a tendency to aggregation of particles. At the same time, the rate of aggregation of this ultrafine system is small, the colloidal solution does not undergo changes for a long time, and it can be considered conditionally kinetically stable (metastable). The rate of aggregation of particles decreases with increasing acidity of the solution. By the sedimentation method in the gravity field it was established that the particle sizes are in the range of 0.7-6.2 microns. In addition, it was found that the dispersion of the system changes during the extraction process, while the particle sizes decrease by the end of the extraction process and the range of particle sizes narrows.

The solution of this scientific problem can be used to create a new generation of dosage forms with higher bioavailability.
SOLVATION OF THE MONOMER UNITS OF LIGNIN IN SUPERCRITICAL CONDITIONS. COMPUTER SIMULATION

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Lignin is one of the most common biopolymers in nature. Due to the abundance of active functional groups in the structure and its physicochemical properties, it is ideally suited as a raw material for the production of various valuable materials. The molecular structure of natural lignin is branched, it is an aromatic heteropolymer formed by radical polymerization of guaiacil, syringyl, various hydroxyphenyl units linked by β-ether, biphenyl and heterocyclic bonds. To date, not much experimental data on the structure of lignin have been obtained, since the strong dependence of the molecular structure of lignin on the parameters of the state, nature and concentration of solvents makes it difficult to study it by experimental methods. In addition, the difficulties associated with experimental studies under supercritical conditions make a computer experiment an acceptable approach to the study of lignin.

In this work, the behavior of model lignin molecules in an aqueous ethanol solution under sub- and supercritical conditions has been studied using classical molecular dynamics simulation. A 2-methoxy-4-(2'-hydroxypropyl)phenol molecule capable of forming a β-O-4 bond with another molecule was taken as a model for lignin. 2-methoxy-4-(2'-hydroxypropyl)phenol is one of the basic structural units of coniferous lignin and goes into solution as a result of its depolymerization in sub- and supercritical water-ethanol mixtures. Water – ethanol mixtures with a mole fraction of ethanol of 0.020, 0.115, 0.285 at T = 573 K and densities of 0.737, 0.708 and 0.612 g / cm³, respectively (the density value corresponded to the experimental pressure of 23 MPa) were researched as a solvent. The potential of TIP4P was chosen for water, a rigid model with parameters from the OPLSAA force field [1] was taken for ethanol. Molecular dynamics modeling was performed in the NVT ensemble.
using the Gromacs-5.0.7 software package [2]. Calculations were performed for systems containing 8 model units of lignin and up to 6000 solvent molecules (water and ethyl alcohol). The duration of observation of the behavior of model lignin molecules and data collection for subsequent analysis of the structural and dynamic properties of the simulated systems was up to 10 ns.

The numerical parameters characterizing the distribution of components in the fluid bulk and in the solvation shell of the solute were obtained. The number of hydrogen bonds formed by the solute with ethanol and water was determined, and tendencies toward preferred solvation were analyzed. Local self-aggregation of ethanol in a subcritical water medium was researched. It is shown that the molecules of the solute are distributed in the solution and do not tend to associate, which is consistent with the experimentally known fact that the polymer structure of lignin in the subcritical aqueous ethanol medium is destroyed and the result is a solution containing monomeric compounds.

*This work was supported by the Russian Foundation for Basic Research, Grant No. 18-29-06072.*

**References**


The efficiency of the process of extraction of hydrocarbons from oil sludge and the content in the extract of undesirable substances, such as sulfur, are determined primarily by the solubility of the components of the oil sludge in the used extractant. As a result, to optimize the proposed technological solutions for the separation of hydrocarbons from oil sludge, making and scaling the laboratory process to a commercial level, information is needed on the thermodynamic and thermophysical properties of systems involved in the process. This led to the study of phase equilibria of such components of oil sludge as naphthalene, sulfur and water with a propane / butane extractant.

Naphthalene is an aromatic hydrocarbon that is part of the oil sludge. As a result of studying the phase equilibrium of the naphthalene-propane / butane system (Fig. 1) using a high-pressure optical cell, its affiliation to type I phase behavior (according to D.F.Williams classification) was established.
In the course of the extraction of hydrocarbons from oil sludge, sulfur and its compounds, to one degree or another, determined by the regime parameters of the process, are included in the composition of the recovered oil product.

Reliable data on the characteristics of the phase equilibrium of this system and the solubility of sulfur in a propane / butane solvent, in particular, can indicate the conditions for minimizing this undesirable substance in the resulting petroleum product.

The phase behavior of the binary system “sulfur-propane / butane” (Fig. 2) can be attributed to the behavior of type 5. In this case, in the region of the supercritical parameters of the propane / butane mixture for the sulfur-propane / butane system, the liquid-vapor phase boundary is maintained and there is a methodical possibility to study the solubility of sulfur in supercritical propane / butane. The results of the study of the solubility of sulfur in propane / butane, carried out in the temperature range of 130-170 ° C, are presented in Figure 3.
The phase behavior of the water–propane / butane binary system (Fig. 4) can be attributed to type 5 behavior. Studies were conducted in the temperature range of 130-170°C.

*The research was carried out at the expense of a grant from the Russian Science Foundation (project No. 19-73-10029)*
SMALL-ANGLE LASER LIGHT SCATTERING IN CRITICAL CARBON DIOXIDE: THEORY AND ANALYSIS OF EXPERIMENT

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The measurement of small-angle laser light scattering in critical CO$_2$ performed in [1] (2008) represents our experimental data which do not fit neither Ornstein – Zernike theory [2,3] nor diffusive multiple scattering model [4]. The authors of [1] partly described their results using the model of a single light scattering in spherical droplets medium, but they were forced to assume that the droplet radius decreases as the medium approaches its critical point. This assumption contradicts the droplet model of critical state.

In this paper we calculate the Poynting vector for small-angle single scattering of monochromatic light by CO$_2$ molecules near the CO$_2$ critical point. The main difference from traditional calculations [2,3] is that we take into account that before and after the scattering event light propagates in the randomly inhomogeneous critical medium. As critical density fluctuations result in local perturbations of refractive index, we replace geometrical path by the optical one while calculating phases of the scattered light waves. Such an approach seems to be a reasonable compromise when describing the light scattering in critical media, where the single scattering approximation does not seem sufficient [4], and the correct accounting for multiple scattering makes the theory too difficult to analyze experimental data.

As the result we get the angular distribution of the critical opalescence intensity that fit well the results of [1]. Unlike [2,3] our result reproduces the longitudinal component of the speckle: speckle image is specific for light scattering in randomly inhomogeneous media and it was observed in [1]. Our formula has proper $\lambda^{-2}$ dependence on the incident light wavelength $\lambda$ and is in agreement with the
traditional view that approach to the critical point is related with the increase in the space correlations length and the variance of density fluctuations.

As in case of the experiments on critical broadening of the vibrational bands of the Fermi-dyad CO$_2$ [5, etc.], the analysis of [1] data does not show the divergence of the critical density variance, but gives its value be very small.


Currently, in the world, proven reserves of coal and hydrocarbon raw materials are $1.963 \times 10^{12}$ tons. $5.23 \times 10^{12}$ tons of oxygen is required to burn this amount of raw materials. Thus, 99.53% of oxygen will remain unused in the atmosphere, relative to currently available $(1.066 \times 10^{15}$ t). This should lead to optimistic forecasts for the future use of the carbon economy. However, a continuous increase in CO₂ in the atmosphere can cause a greenhouse effect, which will change the climate on the Earth's surfaces significantly.

One of the alternative ways to reduce emissions of greenhouse gases into the atmosphere, as well as to solve the predicted problem of shortage of oil in the near future, may be the creation of production of biodiesel fuel (BD) from renewable raw materials, which does not violate the established balance of substances in the biosphere.

Currently, BD is obtained by transesterification of oils or fats with alcohols: methanol or ethanol in the presence of a catalyst, alkali. The transesterification reaction proceeds at the temperature of from 25 to 100 °C at atmospheric pressure, in an environment of 0.5-1.0 molar excess of alcohol for 6-8 hours.

The most promising direction in the production of a database is the supercritical fluid technology (SCFT). Under supercritical conditions, the process of transesterification of oils is carried out at parameters above the critical point of methanol or ethanol. Under these conditions, it is possible to reduce the stages of database production, the time for the implementation of the process, thus reducing capital and operating costs. The supercritical technology makes it possible to eliminate the stages of pretreatment.
of the initial reagents, the removal of soap and water, which are formed at the final stage of obtaining of BD, as well as the use of catalysts. It should be noted that BD obtained by supercritical transesterification of the oil is characterized by high purity of methyl esters, as well as glycerin, which is formed as a by-product.

A flow-through supercritical unit was manufactured to implement the process of supercritical transesterification of oils. The flow rate of SC installation is largely determined by the design of the flow reactor and the principles that ensure the thermal conditions of the transesterification process. Preliminary studies were carried out to optimize the physical parameters of the supercritical flow installation. The process of transesterification of the oil was carried out at the following parameters: temperature - 320-350 °C; pressure - 25-30 MPa; the molar ratio of ethanol to oil - 18-12, time - 25 minutes. Under these conditions, the system overcame the energy barrier, beyond which an 80-fold increase in the reaction rate constant, relative to the subcritical conditions of the process, occurred.

In this regard, it should be noted that according to the literature data, the apparent activation energy of the transesterification reaction to the supercritical state is 56 kJ/mol, whereas under subcritical conditions it is 11.2 kJ/mol (below 240 °C) [1]. Attention should be paid to the fact that at high temperatures required for the efficient transesterification of saturated fatty acids, carrying out the reaction with unsaturated fatty acids might be accompanied by their destruction.

A significant role on the efficiency of the transesterification reaction is exerted by increased pressure; it increases the likelihood of interaction between the molecules of the oil and the alcohol, thus providing the best contact of the reaction mixture, thereby increasing the rate of the reaction.

When implementing the Green Technologies based on supercritical environments, it was shown that environmental safety depends on the introduction of renewable environmentally friendly energy sources, which include BD fuel. To obtain BD fuel, a flow supercritical installation was created allowing the transesterification of oils to be effectively acceptable in terms of thermal parameters. The most promising crops were identified, as well as oil that can be used as BD fuel source in the Republic of Kazakhstan.
References

MODELING OF THE QUASI-ISOTHERMAL FOAMING OF SCF-PLASTICIZED POLYMERS

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Synthesis of highly porous matrices (scaffolds) by foaming of bioresorbable polymers, which are preliminary plasticized using supercritical fluids, is one of the prospective directions in the creation of novel materials for regenerative medicine and tissue engineering. The structure of formed porous matrices substantially depends on not only the physical-chemical properties of the used polymer and plasticizing/foaming agent, but also the scenario of the agent depressurization in the course of foaming. The extreme cases for these scenarios are the quasi-adiabatic free expansion of the foamed volume under the fast depressurization (0.01 MPa/s – 1 MPa/s) and the quasi-isothermal formation of the porous matrix structure under the constant temperature in a super-critical reactor and the slow depressurization (<10^{-3} MPa/s). In the latter case, except the common trend of increase of the bubble sizes under the decrease in the external pressure, a substantial influence on formation of the matrix structure will be caused by processes in the foamed volume, which are characteristic for evolving metastable foams. The dominating process is the gas transfer between neighboring bubbles in the volume and, consequently, the gradual decay in the number of bubbles with the radii lesser than the critical value. On the contrary, it takes place the stable growth of bubbles with the sizes larger than the critical size. Joint influence of the bubble growth under the depressurization and the discrimination controlled by the ratio of the bubble (pore) radius to the critical radius will determine the structural properties of porous matrices formed under the quasi-isothermal foaming. That is why the analysis and modeling of the structure evolution for metastable liquid foams are of a certain interest from the point of view of the development of approaches to control of the supercritical fluidic synthesis of porous matrices.
In this work, we present the results of modeling and analysis of the self-similar evolution of bubble ensembles in metastable liquid foams using the solutions of the non-linear Fokker-Planck equation. The obtained self-similar solution is compared to the experimental data obtained using the image analysis of the subsurface bubbles. In addition, the modeled data are compared to the empirical results obtained using x-ray tomographic analysis of evolving liquid foams [1]. The size distributions for subsurface and bulk bubbles in the model liquid foams (Gillette Shaving Cream) are described with an appropriate accuracy by the self-similar solutions of the non-linear Fokker-Planck equation for various values of the time lapse and temperature. It is established that the temperature-dependent behavior of the scale coefficient in the power-law dependence of the average bubble radius on the time lapse can be adequately described using the Arrhenius equation.

The obtained results of modeling will be used for interpretation of empirical data on the quasi-isothermal foaming of polylactides, which are plasticized using subcritical/supercritical carbon dioxide.

*This work is supported by the RFBR grant # 18-29-06024.*

RESEARCH OF SOLUBILITY OF PHENOLIC CONNECTIONS IN SUPERCRITICAL FLUID ENVIRONMENTS


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Phenolic connections - substances of the aromatic nature which contain one or several hydroxyl groups - OH connected with atoms of carbon of an aromatic kernel. Often this group of connections is called vegetable phenols as the most part of aromatic natural derivatives contains phenolic function or it is formed of phenolic connections, and these connections, as a rule, are produced by plants. The presented report united in itself two works where phenol and tannin were chosen as objects of our researches.

The simplest representative of phenolic connections is phenol from which they also received the name. Solubility of phenol in supercritical carbon dioxide is well studied that it is impossible to tell about propane - butane mix. Within the solution of tasks of utilization of oil slimes this solvent represents a great interest. Researches of solubility were conducted by a static method, using an optical cell. New experimental data of solubility of phenol in propane - butane mix were as a result obtained and the phase chart is constructed.

Tannins possess tannic properties and the characteristic knitting taste. Treat group of the phenolic connections of a phytogenesis containing a large number of groups - OH. Unlike phenol, solubility of tannin is a little studied, but causes interest within extraction of vegetable raw materials and preliminary processing of tea raw materials in supercritical fluid environments. Researches were conducted by a dynamic method and, as solvent, carbon dioxide was used.

Work was performed with financial support of the Russian Science Foundation (RSF) within a grant 18-19-00478 and the Ministries of Education and Science within a state task 13.5112.2017/8.9.
MOLECULAR DYNAMICS SIMULATION OF FERULIC AND SYNAPIC ACIDS IN SUPERCRITICAL CARBON DIOXIDE MODIFIED WITH ETHANOL AND WATER

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Supercritical (SC) fluid extraction is one of the modern methods used to obtain hydroxycinnamic acids and other phenolic compounds from plant sources. Supercritical CO\(_2\) is widely used as a medium in SC processes due to such properties as low toxicity, inertness, environmental safety, low cost and low critical parameters. As ferulic acid (FA) and synapic acid (SA) are the polar compounds, their solubility in scCO\(_2\) is very low, which is between 0.08×10\(^{-5}\) and 2.45×10\(^{-5}\) (mole fraction) at the temperatures from 313 to 333 K and pressures from 10 to 30 MPa for FA, for example [1]. Therefore, in order to extract hydroxycinnamic acids efficiently, the addition of polar cosolvent is needed. R. G. Bitencourt and coauthors [2, 3] had previously reported the solubility of ferulic and caffeic acids in scCO\(_2\) modified by ethanol and water. It was shown that the using of small amounts of ethanol or the ethanol/water mixture as a cosolvent produced a considerable increase in the acids solubility compared to pure scCO\(_2\). The features of intermolecular interactions in such multicomponent systems based on scCO\(_2\) are the subject of discussion in this work.

Using the method of classical molecular dynamics implemented in the software GPU accelerated package Gromacs-5.0.7, the simulation of binary (FA-scCO\(_2\), SA-scCO\(_2\)), ternary (FA-ethanol (3% and 6%) - scCO\(_2\), SA-ethanol (3% and 6%) - scCO\(_2\)) and four-component systems (FA-ethanol (3%) / water (1%) - scCO\(_2\), SA-ethanol (3%) / water (1%) - scCO\(_2\)) was carried out in an isobaric-isothermal ensemble. A constant temperature of 323 K and a constant pressure of 30 MPa were maintained using a v-rescale thermostat and Parrinello-Raman barostat, respectively. After energy minimization and equilibrium, the production run simulations were performed for 10 ns with time step 1 fs and data were recorded for subsequent statistical analysis every
0.1 ps. The calculation of the free energy of solvation was carried out using the Bennett’s acceptance ratio method.

According to the simulation results, the following characteristics were calculated: the local mole fraction of the cosolvent around the solute, the average hydrogen bond (HB) number of the mixture components, the fraction of molecules with i-HBs, the HB distribution over individual solute atoms, the spatial distribution functions of cosolvent around functional groups of the acids, the free energy of solvation.

Analysis of the data shows that the preferential solvation with ethanol is the same for both acids. Small differences in the magnitudes of the maxima are due to the different structure of the molecules, namely, the presence of the methoxy group in the third position of the benzene ring in the SA hinders the localization of ethanol molecules near the hydroxyl group, which is a potential center of hydrogen bonding. The main difference in local surrounding of SA and FA is observed in the systems contained ethanol-water mixture as a cosolvent. Unlike FA for SA the local mole fraction of water around the solute exceeds the local mole fraction of ethanol. This leads to the fact that SA is more solvated by cosolvent molecules in case when ethanol/water mixture is used for modifying scCO₂ than in ethanol-modified scCO₂ although the bulk mole fraction of the cosolvent is higher in the latter case.

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REFERENCES


ALL ATOM MOLECULAR DYNAMICS STUDY OF POLY(METHYL METHACRYLATE) / SUPERCRITICAL CO\textsubscript{2} SYSTEM

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Against the background of the abrupt development of supercritical fluid technologies (SCFT), such processes in polymer / SCFT systems as polymer swelling and irreversible transformation of its native structure, plasticization of polymers in SCF and the molecular mechanism of sorption of scCO\textsubscript{2} and drug compounds into polymer matrices have not been fully established until now. It complicates the development and optimization of relevant technologies. This paper focuses on the structural and dynamic properties of a binary system containing atactic poly(methylmethacrylate) (PMMA) and supercritical carbon dioxide. The choice of PMMA as an object of the study was determined by several factors: the biocompatibility of PMMA and widespread use in medicine, the availability of extensive experimental data on the sorption of scCO\textsubscript{2} in PMMA matrices, and a low glass transition temperature compared to other polymers.

Using the classical molecular dynamics method and the OPLSAA force field, the PMMA / scCO\textsubscript{2} system was simulated in an NPT ensemble. A constant temperature of 333 K and a pressure of 20 and 25 MPa were maintained with the help of a Nose-Hoover thermostat and a Parrinello-Raman barostat, respectively. The cubic cell with periodic boundary conditions contained 27 PMMA molecules (polymerization degree 100, M = 10013.8 g / mol) and 85086 CO\textsubscript{2} molecules. According to the simulation results, atom-atom functions of the radial distribution were obtained, the degree of swelling of the polymer and the mobility of the chains were estimated, the radius of gyration, the mean square displacement were calculated.

This research was supported by the Russian Foundation for Basic Research № 18-29-06008_mk

An experimental study was carried out to obtain biodiesel fuel in the process of transesterification of oil obtained from shea wood in ethanol under supercritical fluid conditions under ultrasonic action on the reacting medium at molar ratios of ethyl alcohol – shea butter 18:1 - 25:1 in the temperature range 623 - 653 K, reaction time 10 - 40 minutes, pressure 30 MPa on installations that implement periodic and flow-through mode. The optimal reaction conditions and the molar ratios of the initial reagents were determined. Evaluation factors in determining the amount of the desired product obtained were chromatographic analysis and "viscous correlation". This correlation of the content of FAEE in samples of the product of the transesterification reaction carried out in SCF conditions is determined as a function of the kinematic viscosity of these samples:

\[ W = A \ln(\nu) + B \]  
\[ \nu = \exp\left(\frac{W}{A-C}\right) \]

where: 
- \( W \) - the concentration of FAEE in the sample of the reaction product, mass. %;
- \( \nu \) –kinematic viscosity of the sample of the reaction product, mm\(^2\)·s\(^{-1}\);
- \( A, B, C \) - fitting empirical parameters.

The values of the constants of equation (2) are determined using a linear approximation of the viscosity-concentration dependence for hypothetical samples of the reaction product in which there is no alcohol component (shea butter and FAEE).

*The authors of this study are grateful to the Committee of Science of the Ministry of Education and Science of the Republic of Kazakhstan in implementing «The «Green» Technologies based on Supercritical environments» (IRN No. BR05236420)*
SCF-TECHNIQUE MODIFICATION OF BIOLOGICAL AND CALCIUM PHOPHATE BONE MATRIXES FOR SURGICAL IMPLANTS
PREPARATION IN AIMS OF REGENERATIVE MEDICINE
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The new advanced technology of preparation of two sets of osteosubstituted matrixes for direct surgical use is the aim of the project. The benefits for regenerative practical medicine are under the work and were planed to be achieved through the use of combination methods based on supercritical fluid solvents. The way is to get to highly increased biocompatibility of prepared matrixes.

Two sets of chemically independent osteosubstituted matrixes for direct in vivo implantation were under preparation and detailed investigation during the first year. The first set is of biological origin from beef bones and the second is synthetic one, synthesized through harden-process of calcium-phosphate cements.

The following characteristics of new biological and calcium phosphate matrixes were achieved and consummated together through the use of methods of SC-technique. These key positions are:

1. Extremely high purity of prepared matrixes and efficient formation of an open porous in matrix systems of both types.

2. As a second principle step the obtained biological matrixes of high purity have been partly incorporated into their porous structure with polylactide polymers.

Small pieces of both types biological matrixes (of previously inaccessibly high purity and that partly covered with polylactides) were successfully tested as numerous under skin implants in rats of Wistar-line. Detailed histological analysis was performed. These first in vivo surgical experiments with no exepition show high biocompatibility of all tested implants.

This research was supported by the Russian Foundation for Basic Research № 18-29-06010_mk.
The aim of the work is to develop a method for predicting the parameters of the thermophysical properties of reservoir fluids and water-oil-gas mixtures of oil fields using data from standard well studies. The process of extracting a reservoir hydrocarbon mixture to the surface is considered. This process is accompanied by a change in pressure and temperature. In this case, as a result, the concentration of its constituent liquid and gas components is changing. For example, a decrease in pressure below the saturation pressure leads to oil degassing, and the presence of water contributes to the formation of water-oil mixtures.

The thermophysical properties of fluids were determined experimentally and analytically near critical points. When performing thermophysical calculations, source data on oil and gas systems obtained from Azerbaijan fields were used. For the calculations we used the computational methods developed by us. The reliability of the calculations was controlled by experimental values of the parameters of the thermophysical properties - coefficients of heat and thermal diffusivity and specific heat capacity. Thermophysical properties of reservoir fluids were determined experimentally and were predicted using analytical methods. The reliability of the calculations was determined by comparing the accuracy of the values with the errors of the experiments. Thermobaric conditions for finding fluids were taken into account.

The concentration fractions of the constituent components of the formation fluids, the type and structure of the hydrocarbon mixture change at different stages of the technology for the development of oil and gas fields. Therefore, when determining
the thermophysical properties of hydrocarbon systems including fluids, the concentration fractions of the components contained in the fluids were taken into account. The thermophysical properties of fluids near critical points were approximated by correlation dependences. The results were compared with the data of PVT (pressure, volume, temperature) research.

Acknowledgments.

Research has been partially financial supported by the SOCAR Science Foundation (project № 12LR – AMEA).
The aim of this work is the selection and analysis of thermodynamic models for successful correlation of equilibria in hydrocarbon mixtures and fluids near critical points. The use of thermodynamic-mathematical models is important, for example, when using simulators describing the processes occurring in oil and gas formations. Such models allow to adequately reproduce the PVT properties, in particular, fluids in a wide range of pressures and temperatures, taking into account the features of the studied objects of development.

To create adequate PVT-models of hydrocarbon systems we used data based on the results of laboratory and field research. Hydrocarbon systems were used as input data for creating a PVT model and for its subsequent adaptation.

For the PVT model, parameters were set, such as critical properties of fractions, for example, the C6 + group of the mixture, the pair interaction coefficients, and the shift-parameters of components. Taking into account the adjustment of the parameters, the PVT models reproduced the properties of the natural hydrocarbon systems of oil and gas condensate fields of Azerbaijan.

We have corrected the equations of multiphase equilibrium and modified thermodynamic models of solutions to calculate the characteristics of the vapor-liquid and liquid-liquid systems.

In the framework of the models of regular and quasichemical solutions for binary systems, formulas for calculating excess
Gibbs free energy and activity coefficients are obtained. Thermodynamic characteristics, excess Gibbs free energy, and activity coefficients of components of hydrocarbon-containing systems and fluids near critical points were calculated.

**Acknowledgments.**

Research has been partially financial supported by the SOCAR Science Foundation (project № 12LR – AMEA).
EXTRACTING BIOLOGICALLY ACTIVE SUBSTANCES FROM MILK THISTLE SUPERCritical FLUID EXTRACTION WITH CARBON DIOXIDE

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Milk thistle (м. thistle) is used in folk and scientific medicine not accidentaly. This plant is rich in powerful natural hepatoprotectors and fatty oil. Flavolignanov complex of this plant is used in caring of diseases of liver, pancreas, spleen, etc. Fatty oil is used both to regenerate the skin, and as a cholesterol lowering agent. Meal is used as a biological active additive due to the content of a large amount of amino acids, micro-and macronutrients. On the territory of the Republic of Dagestan (RD) it is distributed everywhere, except mountainous areas. It mainly grows in abandoned arable land, pastures, along roads and in vegetable gardens. Before extracting flavolignan fruits м. thistle is degreased with organic solvents or cold pressing. The first method leads to residual toxicity of the product, the second is not effective because extraction of oil from the matrix of raw materials is not complete. An alternative method is supercritical fluid extraction with carbon dioxide, which is a safe and comprehensive method for extracting oil and other biologically active substances. The extract obtained in this way can be a complete product on the pharmaceutical and cosmetic market, bypassing the solvent removal stage.

In the literature there is no data on the composition of fatty oil of the fruit of the м. thistle Dagestan origin. For the first time, a CO$_2$ extract of fruits м. thistle was obtained and analyzed, growing on the territory of RD.

The extraction process was carried out at a temperature of 40 °C, a pressure of 400 bar, a flow rate of carbon dioxide of 50 g / min, an extraction time of 60 minutes. The extract is a fatty oil of light yellow color with inclusions of white wax with a density of 0.9265 g / ml, refractive index 1.4716. The content of fatty oil in the fruit on the territory of RD (25%) is lower than in the cultivated in the region Samara (28%) [1].
Before determining the fatty acid composition, the resulting oil was subjected to hydrolysis according to the method GOST R 51486 [2]. To do this, 10 ml of potassium methylate were added to 1.0 g of oil and heated in a water bath under reflux for 15 minutes. Then, 13 ml of 5% hydrochloric acid in methyl alcohol was poured. Heated for 10 minutes. The resulting mixture was cooled and extracted with hexane and washed until the acid was removed. Fatty acid methyl esters were determined on an Agilent Technologies 7820A GC System Maestro gas chromatograph equipped with an Agilent Technologies 5975 Series MSD mass selective detector with electron impact ionization, ionization energy 70 eV. The compounds were identified by comparing experimental mass spectra with library (Wiley275 and NIST98) mass spectra. The total content of flavolignans in oil m. thistle was determined spectrophotometrically using a SPECORD 210 Plus BU spectrophotometer (Analytik Jena, Germany). 95% ethyl alcohol was used as an extractant [3].

The results of the analysis showed that the oil obtained by supercritical fluid extraction contains triglycerides of linoleic (64 ± 2%), oleic (23 ± 1%), palmitic (7.7 ± 0.4%), stearic (3.0 ± 0, 2%), arachidic (1.5 ± 0.7%) and myristic acid (0.17 ± 0.06%). The total content of essential omega-6 (linoleic acid) and omega-9 (oleic acid) in the oil from the fruit p. spotty is about 85%. The content of flavolignans in oil is 2.6 mg / g.

In the future, it is planned to study the effect of physical parameters on the yield and quality of the extraction product.

**Literature:**


2. GOST 31665-2012, vegetable oils and animal fats. Preparation of fatty acid methyl esters.

QUANTUM-CHEMICAL SIMULATION AND ORBITAL SPECIFICITY (WITHIN THE WOODWARDS-HOFFMAN RULE) OF PARTICIPATION OF OXYGEN AND WATER TRIPLETIC ASSOCIATES IN THE PROCESS OF SUPERCritical WATER OXYDATION

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Using the Woodward-Hoffman rule, the orbital specificity is described and quantum-chemical simulation in the Gaussian09 software package using the DFT method the interaction of $^3O_2$ and $^1O_2$ are modeled, as well as the triplet associates of oxygen and water with hydrogen, hydrocarbons and 2,3-dihydronaphthalene.

It is shown that in the case of the orthogonal arrangement of the triplet oxygen bond and a simple carbon-hydrogen bond, the interaction of the orbitals satisfies the Woodward-Hoffman rules, which makes the direct participation of $^3O_2$ in oxidative dehydrogenation real. However, this does not apply to molecular hydrogen due to the small size of the proton and the length of the H – H bond, for this reason, the transition state is not localized for the direct interaction of $^3O_2$ with H$_2$. However, for the direct effect of $^3O_2$ on the primary C – H bond of propane, a transition state was localized corresponding to the process of radical detachment of the hydrogen atom from the hydrocarbon.

Also, the initial stages of oxidation in oxygen-water-hydrogen or hydrocarbon reaction systems were quantum-chemically studied. As a result of the calculations, direct oxidative dehydrogenation is energetically more preferable in comparison with the hydration direction, and also the hydrate stabilization of the hydroperoxyl radical takes place.
Acknowledgments

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References

THE PLANT FOR SUPERCritical WATER OXIDATION AND ITS USE IN WASTE WATER NEUTRALIZATION AND PURIFICATION OF ULTRA-DISPERSED DIAMONDS


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The technology of supercritical water oxidation (SCWO) is of great interest to solve the problem of industrial neutralization of toxic wastes and of cleaning industrial products.

A pilot SCWO flow-through production plant was developed at JSC “Federal Research and Production Center “Altai” where the tests for neutralization of organic industrial wastes and for cleaning aqueous suspensions of ultra-dispersed diamonds were carried out.

The plant consists of a high-pressure metering pump for waste water, a compressor to supply compressed air, an electric water and air heater, a tubular reactor with an operating volume of 5.7 liters, a cooling device and a device for output pressure relief. The plant capacity as for waste water is up to 30 l/h. The operating parameters are the following: temperature is 650 - 700 ºC, pressure is 23 - 29 MPa. They provide conditions for water transition into the supercritical state with unlimited solubility of any organic substances and oxygen, and high oxidation rates of these substances.

A high efficiency of waste water neutralization was previously shown in operation of SCWO plant with waste water from the nitroglycerin and diethylene glycol dinitrate production. The decomposition degree for those substances was achieved to be no less than 99.93%.

Further tests were carried out for neutralization of waste waters generated at the pilot plant operating at JSC “FR&PC “Altai” to produce various organic substances. Approximate composition of wastes are dimethylformamide - 65-75%; acetic acid - 15-25%; ethanol - 4-10%; toluene - 2-5%; water - up to 8%; ammonium nitrate - up to 4%; ammonium sulfate - up to 250 mg / l. The behavior of ammonium nitrate
containing up to 60% of oxygen under supercritical conditions for water was not studied, especially in the presence of combustible substances. To avoid an uncontrollable oxidation process, its amount was limited to 3%. The wastes of the above composition in the amount of 8.0 - 9.1% were put into the water.

The results of wastes neutralization were assessed by COD values, the content of nitrates, nitrites and ammonia nitrogen in the water samples taken from the reactor. Table 1 shows the results of one of several experimental series.

Table 1 – Waste neutralization results

<table>
<thead>
<tr>
<th>Indicator</th>
<th>Before neutralization</th>
<th>After neutralization</th>
<th>The time of sampling from the process start-up, min.</th>
<th>The degree of neutralization, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>COD, mgO2/l</td>
<td>95277,8</td>
<td>119,9</td>
<td>15</td>
<td>99,87</td>
</tr>
<tr>
<td></td>
<td>95277,8</td>
<td>128,1</td>
<td>37</td>
<td>99,86</td>
</tr>
<tr>
<td></td>
<td>95277,8</td>
<td>103,5</td>
<td>65</td>
<td>99,89</td>
</tr>
<tr>
<td>Ammonia nitrogen, mg/l</td>
<td>3206,4</td>
<td>5000,3</td>
<td>15</td>
<td>increase 55,9 %</td>
</tr>
<tr>
<td></td>
<td>3206,4</td>
<td>143,0</td>
<td>37</td>
<td>95,5</td>
</tr>
<tr>
<td></td>
<td>3206,4</td>
<td>231,4</td>
<td>65</td>
<td>92,8</td>
</tr>
<tr>
<td>Content of nitrates, mg/l</td>
<td>9728,0</td>
<td>1,11</td>
<td>15</td>
<td>99,99</td>
</tr>
<tr>
<td></td>
<td>9728,0</td>
<td>0,37</td>
<td>37</td>
<td>99,99</td>
</tr>
<tr>
<td></td>
<td>9728,0</td>
<td>0,86</td>
<td>65</td>
<td>99,99</td>
</tr>
<tr>
<td>Content of nitrites, mg/l</td>
<td>23,49</td>
<td>1,34</td>
<td>15</td>
<td>94,3</td>
</tr>
<tr>
<td></td>
<td>23,49</td>
<td>0,64</td>
<td>37</td>
<td>97,3</td>
</tr>
<tr>
<td></td>
<td>23,49</td>
<td>0,49</td>
<td>65</td>
<td>97,9</td>
</tr>
<tr>
<td>pH</td>
<td>3,85</td>
<td>7,95</td>
<td>15</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>3,85</td>
<td>7,02</td>
<td>37</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>3,85</td>
<td>7,24</td>
<td>65</td>
<td>-</td>
</tr>
</tbody>
</table>

In all the operations, the degree of organic substances oxidation is over 99%. Nitrates decompose completely; nitrites are not formed because of nitrates decomposition. The ammonia nitrogen content at the beginning of the process increases due to the decomposition of dimethylformamide (75% in the wastes), ammonia being oxidized when the process becomes stable.

Another application of SCWO pilot plant is to purify ultra-dispersed diamonds (UDD) from oxidizable carbon forms. For the research, some UDD-B product produced at JSC “Federal Research and Production Center “Altai” was used. The characteristics of UDA-B are the following: solids content in the aqueous medium is 1.1% (by weight); oxidizable impurities content is 3.9% (by weight); non-combustible impurities content is 2.6% (by weight).
The oxidation was carried out with the addition of hydrogen peroxide to the aqueous suspension of 10:1 by volume. The results of UDD-B treatment in SCWO plant showed a decrease from 3.9% to 1% in oxidizable impurities content, while non-combustible impurities content remained unchanged. Thus, the given test results showed a high efficiency of SCWO processes when neutralizing industrial waste products and purifying ultra-dispersed diamonds from oxidizable forms of carbon in the presence of hydrogen peroxide. A higher performance unit is suggested to be developed.
THE STUDY OF SUPERCRITICAL EXTRACTS FROM PLANTS

NICOTIANA TABACUM L


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It is known that the composition of plant extracts depends on a number of factors: temperature, extraction time, the ratio of vegetable raw materials / extractant and, of course, the main factor is the nature of the solvent used or the solvent system.

For chemistry, one of the most promising methods for processing the processing of plant materials is the extraction of supercritical carbon dioxide. Its critical temperature (31°C), therefore, biological materials can be processed up to 60 °C, which does not lead to their thermal destruction. Density and solvation characteristics of supercritical CO₂ at close to hexane; thus, it acts as a non-polar solvent.

As a plant material, we chose the plant Nicotiana tabacum L., due to the high content of biologically active substances in the leaves of tobacco.

The aim of the work was to study the qualitative and quantitative composition of the extracts obtained.

The supercritical extraction method was carried out on a Thar SFE-1000 CO₂-extraction unit under the following conditions: the temperature in the reactor was 28°C, the pressure of CO₂ was 150 bar.

The extract obtained was investigated by gas chromatography on an Agilent Technologies 7890N / 5973N GS / MS gas chromatograph with a mass selective detector. Components were identified by mass spectra and retention times using the NIST library and Wiley GC / MS.

A high content of organic acids, in particular, sorbic and benzoic acids, is noted in the supercritical extract, and a greater number of compounds are also isolated. 31 compounds are identified in the hexane extract, while in the carbon-dioxide supercritical - 70 compounds. The content of the main product of extraction, namely
nicotine, was 19.34%, which is almost identical to the content in the extract obtained by the traditional method of solvent extraction.

Further we increase the yield of nicotine; we increased the process temperature from 28 to 60°C.

As a result of the increase in temperature while maintaining the pressure, we observe a significant increase in the efficiency of nicotine extraction by 23.70%, while in previous processes the yield was less than 20%; also compared with supercritical extraction at low temperatures, we note a smaller number of identified compounds - 42, against 70, in addition to the extract obtained in the process with heating, in addition to nicotine, a large number of compounds belonging to the groups of alcohols and ethers, while in the process without additional heating, more organic acids were identified. These changes in composition are explained by the fact that in supercritical processes, pressure and temperature are of decisive importance not only on the completeness of extraction.

As a preferred process for extracting nicotine from tobacco, we propose a supercritical process with heating up to 60 ° C and a pressure of 150 bar, since in terms of product yield it significantly surpasses the classical liquid extraction with an organic solvent and the supercritical process without heating, however, increasing pressure does not lead to an increase in completeness extraction, this stems from the very principle of supercritical extraction and the direct dependence of the degree of solvation of various groups of BAS on pressure, we have established this fact for following the extraction at a higher pressure (170 bar), but receiving a lower degree of extraction, only 12.29%, while at 150 bar the extraction reached 23.70%, which is almost twice as high.

In this paper, we first conducted a comparative analysis of liquid and supercritical extraction of biologically active substances from the plant *Nicotiana tabacum* L, harvested in the Republic of Kazakhstan.

For the first time, optimal values of pressure and temperature have been established for nicotine release by supercritical fluid extraction with carbon dioxide.

For the first time, the qualitative and quantitative composition of extracts obtained by supercritical fluid extraction with carbon dioxide at various pressures and temperatures has been established.
EFFECT OF PRESSURE ON THE EFFICIENCY OF NICOTINE EXTRACTION FROM PLANTS NICOTIANA TABACUM L


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The plant Nicotiana tabacum L is well known as an industrial source of nicotine, which is due to the high content of (S)-3-(1-methyl-2-pyrrolidinyl) pyridine in tobacco leaves, reaching up to 5% of the weight of dry plant material in some varieties.

Methods of highly efficient extraction of nicotine from plant raw materials are due to the increased demand for nicotine-containing drugs, which act as an alternative to tobacco and are used in the process of quitting smoking.

The aim of the work was to study the qualitative and quantitative composition of extracts isolated from tobacco harvested in the Almaty region of the Republic of Kazakhstan. The extract is obtained by the method of supercritical fluid CO₂-extraction.

The supercritical extraction method was carried out on a Thar SFE-1000 CO₂-extraction unit under the following conditions: the temperature in the reactor is 60 °C, the pressure of CO₂ is 120, 150 and 170 bar.

The extract obtained was investigated by gas chromatography on an Agilent Technologies 7890N / 5973N GS / MS gas chromatograph with a mass selective detector. Components were identified by mass spectra and retention times using the NIST library and Wiley GC / MS.

In a supercritical extract extracted under conditions of 120 bar and a temperature of 60 °C, it was possible to achieve an extremely high yield of nicotine, which is 47.40%, and this is a very high figure for alkaloids.
Note that in addition to nicotine, its derivatives have been identified: cotinine and nicotine.

In addition, in the extract obtained under these conditions, the largest number of compounds (125) was identified. But almost all of them, except for phytol acetate, are present in minor quantities.

In the extraction process, carried out under the conditions of 150 bar and 60 °C, there is a significantly smaller amount of nicotine of 23.70% compared with supercritical extraction at lower temperatures. In this case, a smaller number of identified compounds is noted (42, versus 125). In addition, in the extract obtained in the process with heating, in addition to nicotine, a significant amount of compounds belonging to classes of organic esters and hydrocarbons such as: 2-cyclohexen-1-one, 4- (3-hydroxy-1-butenyl) - 3,5,5-trimethyl, 5- (decahydro-5,5,8a-trimethyl-2-methylene-1-naphthalenyl) -3-methyl 2-pentenoic acid ester, 4,8,13-cyclotetradecatriene-1,3 -diol, heptacosan, glycerin 1-palmitate, gentriacontan and triacontan. It should be noted that the content of these compounds is more than 2%, is of practical interest.

Next, we carried out the extraction process at a higher pressure while maintaining the same temperature values, namely, 60 °C at a pressure of 170 bar.

In the results of the analysis of the extract obtained at elevated pressure and temperature, we see a significantly smaller amount of extracted nicotine (12.29%), while in this extract nicotine is not the dominant compound, since the content of acetic acid butyl ester (14.36%), sorbic acid (15.76) and benzoic acid (28.81%) are significantly higher, the total number of identified compounds is less, only 28. This is due to a significant change in the solubilizing properties of carbon dioxide due to the increase in pressure.

The carried out and analyzed modes of SCF extraction allow us to draw the following conclusions:

- An increase in pressure leads to a change in the properties of the solvent and does not cause degradation processes. This is evidenced by the analysis of the chemical compositions of the obtained extracts: at a relatively high temperature for a BAS, substances of rather complex composition were identified. The
reason for this may be the absence of an oxidizing agent in the system and a short heating time;
- Degree of extraction of nicotine at a pressure of 170 bar and a temperature of 60 °C extracts the smallest amount of alkaloids and the greatest organic acids;
- With the extraction mode of 150 bar and a temperature of 60 °C, the largest amount of hydrocarbons and organic esters is extracted;
- As a preferred process, we propose a supercritical process with heating up to 60 °C and a pressure of 120 bar, at which the nicotine extraction rate reached 47.40% . For this parameter, it is far superior to the other extraction options we considered.
COMPARATIVE STUDY OF THE FAT-ACID COMPOSITION OF OILS OF SEEDS OF TOMATO “ASTRAKHANSKY”, OBTAINED BY COLD CUT AND SUPERCRITICAL FLUID EXTRACTION

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Tomato seeds in large quantities are formed as waste in the processing of tomatoes to produce products such as tomato juice, sauce and pasta. One of the possible applications of these seeds is to obtain vegetable oil from them, which is a valuable source of unsaturated fatty acids.

The aim of the study was a comparative study of the fatty acid composition of oils obtained from the seeds of tomato varieties "Astrakhansky" by cold pressing and supercritical fluid extraction. Supercritical extraction with carbon dioxide (sc-CO₂) of oil from tomato seeds was carried out by varying the temperature, pressure and duration of extraction. It was established that the greatest yield of oil (95%) is observed at a pressure of 30 MPa, a temperature of 50 °C and duration of the extraction process of 2 hours.

The quantitative determination of fatty acids was carried out by gas chromatography – chromatography-mass spectrometry after transferring the fatty acids to the corresponding methyl esters by treating the oil with a solution of diazomethane in diethyl ether according to the procedure given in [1].

It was established that the main components of cold-pressed tomato oil were linoleic (C18:2) (53.62%), oleic (C18:1) (22.23%), palmitic (C16:0) (14.1%) acids. At the same time, tomato oil, obtained by supercritical fluid extraction, has a high content of linoleic acid (56.32%), arachidonic acid (2.75%) and a lower content of stearic acid (C18: 0).

As minor components in tomato oil obtained by two methods, cis-9-eicocenic acid (C20: 1), docosahexaenoic acid (C22: 6), α-linolenic (C18: 3) acids were identified.

The continuous increase in energy consumption, accompanied by the depletion of natural oil reserves leads to the search and expansion of the resource base, in this connection the involvement in energy and petrochemical synthesis of low-grade fuels of natural origin (brown coal, bitumen, oil shale, peat, sapropel, biomass) is becoming increasingly important [1-3]. The main difficulty lies in the fact that the organic component of low-grade fuels is a multicomponent mixture with a high content of heteroatoms. To vary the properties and reactivity of low-grade natural organic raw materials, use different methods of physical and chemical effects on the feedstock [4]. In the first case, there is a "loosening" of the multi-dimensional structure, in the second, along with the activation, there is a dissolution of low-molecular components located in the pores of the initial substance, and a partial destruction of donor-acceptor bonds existing between macromolecules of organic matter.

Previously, we found that treatment with supercritical carbon dioxide (SC-CO₂) allows to extract large fragments of biologically active substances (proteins, peptides, amino acids, vitamins, hormones, enzymes) from the organic matter of sapropels [5].

The aim of this work was to study the effect of pretreatment of native sapropel with SC-CO₂ on the properties and composition of solid raw materials and to show the prospects of using this method to intensify the hydro-liquefaction process.

It was found that the extraction of sapropels SC-CO₂ (50 °C, 30 MPa) leads to a change in the elemental and group composition of the organic matter, as well as physical-chemical parameters and texture characteristics of raw materials (Fig.1). Pretreatment of sapropel SC-CO₂ proved to be promising for regulating the reactivity
of sapropels for subsequent thermochemical processing to produce liquid hydrocarbons and combustible gases.

It is shown that the pre-extraction of SC-CO₂ sapropels allows to achieve the maximum degree of conversion in the process of hydro-liquefaction at lower temperatures in comparison with raw materials. Analysis of liquid hydro-liquefaction products of pre-extracted sapropels showed a significantly lower content of heteroatomic compounds compared with liquid hydro-liquefaction products of native sapropel.

![Integral pore size distribution in solid samples obtained before (1) and after (2) SC-CO₂ extraction.](image1)

![Temperature effect on the degree of conversion OM sapropel before (1,3) and after (2,4) SC-CO₂ extraction.](image2)


HIGH-POROUS MATERIALS BASED ON ULTRA-HIGH-MOLECULAR-WEIGHT POLYETHYLENE AS A BASIS OF BIOIMPLANTS OF NEW GENERATION

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Highly porous aerogels based on ultra-high-molecular-weight polyethylene (UHMWPE) were synthesized by solvent extraction from the pores of the swollen polymer using supercritical CO₂. Depending on the amount of solvent in the swollen polymer, the resulting UHMWPE-aerogels had a specific surface area of 15–77 m²/g, a density of 0.04–0.1 g/cm³, and had a polymodal pore system.

UHMWPE-based highly porous materials were used to culture SHSY5 human neuroblastoma cells. It turned out that the obtained materials were a very convenient bioinert matrix for cells whose lifetime exceeded 60 days.

A financial support from the Russian Science Foundation (Grant no. 18-13-00145) is greatly acknowledged.
NEW METHODS FOR THE SEPARATION OF HEAVY OILS AND OIL RESIDUES INTO NARROW FRACTIONS USING SUPERCritical CARBON DIOXIDE (SC-CO₂)

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The composition and properties of heavy petroleum feedstock (HPF), in particular, the content of asphaltenes, directly affect on the recovery, transportation and refining of heavy oils and oil residues. It is known that asphaltenes significantly affect on the viscosity of crude oil, its stability and compatibility at storage, mixing and transport. In addition, asphaltenes are carriers and concentrators of heavy metals, carbon residue and heteroatoms that are present in petroleum. Consequently, their content and composition influences the choice and engineering design of upgrading and refining technologies of HPF as well as the yield, composition and properties of products obtained. In turn, separation of non-distilled vacuum residues using the supercritical fluid extraction and fractionation process (SFEF) makes it possible to evaluate the chemical composition of residuum’s fractions with increasing molecular weight, which is important information in terms of both chemistry and geochemistry of crude oil and the choice of bottom of the barrel technology.

Thus, the separation of heavy oils and oil residues with subsequent determination of the yield, composition and properties of resulting fractions is an important analytical task. The conventional extraction methods are based on the use of light n-alkanes as solvents and have a number of obvious drawbacks including the low efficiency, duration, large solvent volumes required and sufficiently high temperatures in the case of oil residue fractionation. It should also be noted that there is no unified approach to the extraction of asphaltenes, and their content and, consequently, composition and properties depend on the type and solvent power of hydrocarbon solvent, which makes it difficult to determine their molecular structure.
In this regard, a promising direction for the development and improvement of methods for the separation of heavy oil and oil residues is the search for alternative solvents permitting overcome the abovementioned disadvantages. One of these solvents may be supercritical dioxide carbon (SC-CO$_2$) having a low critical temperature and being non-toxic, relatively cheap, nonflammable and explosion-proof. SC-CO$_2$ is an effective anti-solvent that facilitate fast and strong coagulation of asphaltene molecules with their subsequent precipitation and destruction of the oil dispersed system. Despite the low solubility of the high molecular components of oil residues in SC-CO$_2$, the addition of organic modifiers to CO$_2$ can significantly increase its solubility revealing the possibility of fractionation and control the yield of extracted fractions by simply changing the modifier concentration in the solvent composition.

The report shows the possibility of separating heavy oils and oil residues using SC-CO$_2$ as an anti-solvent and solvent base. SFEF of samples of heavy oil and vacuum residue was carried out with a gradual increase in the concentration of organic modifier in the solvent flow and continuous separation and collection of extract fractions. The effect of the modifier type on the yield and composition of the extracted fractions for the selected process parameters has been determined. The influence of parameters (temperature, pressure, residence time, addition of a hydrocarbon diluent) on the yield and properties of asphaltene fractions separated from heavy oil in the GAS (Gas Anti-Solvent) process has been established. Comparison of the composition and the yield of fractions obtained by proposed methods with the results of conventional laboratory methods for asphaltene separation and fractionation by distillation has been conducted.

*The work was supported financially by Russian Foundation for Basic Research (№18-33-00716) and Russian Science Foundation (№18-73-00345).*
SUPERCRITICAL HYDROTHERMAL DESTRUCTION OF ORGANIC-CONTAINING WASTES IN THE AIC

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The lack of high-performance, environmentally friendly, energy-efficient technologies for the disposal and recycling of ever-increasing volumes of agricultural waste and processing enterprises of the agro-industrial complex leads to the search for new technical and technological solutions for their processing. A wide range of wastes, differing in the state of aggregation and physicochemical properties, allow us to consider the technology of supercritical hydrothermal destruction (SCHD) as one of the priorities. A distinctive feature of the SCHD technology is the possibility of its implementation in two modes: autothermal oxidation of organic impurities by hydrogen peroxide or oxygen to safe air (CO₂, H₂O, N₂ - using air) and allothermic pyrolysis of organic impurities without oxidant supply.

Supercritical water oxidation (SCWO) is most preferable to use [1] for the destruction of highly hazardous and toxic substances (POPs, including pesticides, halogen-containing transformer oils, etc.) and waste from the agro-industrial complex, including waste of pork and poultry breeding of 3 hazard class. The peculiarity of the waste of the agro-industrial complex is their different aggregative state: solid with different humidity, liquid (suspensions and emulsions with different content of organic substances). The SCWO technology of the POPs group of 1-3 hazard classes, which received a positive conclusion from the state environmental review of Rosprirodnadzor, provides for the supply of initial water-organic mixtures to a reactor with supercritical parameters of the aquatic environment through nozzles with a hole diameter of 200 microns. This necessitates the sample preparation of the initial mixtures with the crushing of solid waste to a fraction of less than 100 microns.
Different humidity of the initial AIC waste from 4 to 96% is not a limiting factor, since water is the medium for the reaction of supercritical hydrothermal destruction carried out in the autothermal or allothermic regimes. Conducted extensive research in the pilot industrial reactor СКГД-10-ЭЭТ (developed by LLC «ЭКОЭНЕРГОТЕХ»), operating in flow and autoclave modes for the disposal of pesticides (DDT, HCCHT, HCB, etc.), wastewater pig farms, beer and alcohol bards, confirmed the effectiveness of their oxidation not less than 99% to hydrogen dioxide and water, occurring within 1.5-2 minutes, without the formation of hazardous components (dioxins, furans, nitrogen oxides).

The allothermic regime of hydrothermal destruction without the use of oxidizing agents ensures the pyrolysis of the organic part of the waste with the formation of combustible gases (CO, H₂, CH₄) with a calorific value of about 10-18 MJ/kg with an initial organic content of 15-25%. Low concentrated organic waste and wastewater (containing 4-6% organic matter) require preliminary operations to concentrate it.

We have shown the possibility of concentrating organic impurities by adsorption and membrane methods [2, 3]. Solid agricultural waste (husks of buckwheat, sunflower, rice) pre-crushed in a knife mill to a fraction of 100 microns was used as an adsorbent. Suspension of these solid wastes with sorbed organic impurities was subjected to supercritical hydrothermal pyrolysis, which allowed simultaneous utilization of two types of AIC wastes (wastewater and plant wastes) to produce energetic combustible gases. At the same time, it is possible to neutralize organic substances (for example, pesticides) that are poorly soluble in water when they are predisolved in waste oils.

When determining the COD of the initial aqueous mixtures and condensate after their SCHD, the dispersion of crushed solid plant waste and other parameters used the existing equipment of the collective scientific center «Nano-Centre» FSBSI FSAC VIM.

Taking into account the characteristics of the gas mixtures formed during autothermal oxidation (temperature - 400 °C, pressure - about 220 atm) and during allothermic pyrolysis (combustible gases), it is advisable to further use their energy potential as
working fluids for obtaining thermal and electrical energy in steam mini-turbines and gas piston power plants.

References


CONVECTIVE TRANSPORT IN PARTICLES OF GROUND PLANT MATERIAL DURING SUPERCRITICAL FLUID EXTRACTION

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One of the applications of the technology of Supercritical Fluid Extraction (SFE) is the extraction of valuable natural compounds (fatty oils) from vegetable raw materials – ground seeds with high initial oil content. Such raw materials are characterized by a high initial content of extractable compounds; thus, the oil phase fills a major part of the cell volume.

It is traditionally assumed that during SFE the solvent — supercritical CO₂ — penetrates into the raw material and dissolves the oil in itself. Extraction is carried out by diffusion transport against the concentration gradient according to the Fick's law. However, this schematization completely ignores the dissolution of CO₂ in the oil phase [1], and suggests that the replacing of the oil phase with the solvent that penetrates the particle does not cause convective transfer. This is natural for multiphase problems.

In the present paper, the oil distribution along the particle is described in terms of the shrinking core approach [2], which takes place at a low conductivity of transport channels compared to the cell membrane [3]. It is assumed that there is an internal “core” filled with the oil phase with CO₂ dissolved in it and an external transport zone through which the oil dissolved in the solvent is transferred to the surface of the particle. Within the framework of this schematization, conditions were determined that lead to a non-zero mean mass transfer rate of the solution in the transport zone.

The intensity of convective transport with respect to the diffusion one is determined by the product of two similarity criteria, Θ and δ. The first one characterizes the oil content of the raw material and is equal to the ratio of the solvent saturation concentration of the target compounds to the initial oil content, and the second is equal to the ratio of the phase densities in the core and the transport zone. The
parameter $\Theta$ for high oil raw materials takes values of the order of 0.01, which at $\delta \sim 1$ leads to a negligible intensity of microscale convective transport.

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OPTICALLY ACTIVE SiO$_2$ AEROGELS: SYNTHESIS OF TRANSITION METAL COMPLEXES

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Aerogels are a class of solid mesoporous materials with high specific surface area and high porosity. Due to such characteristics, aerogels are of great interest for catalysis.

The purpose of this work was to obtain materials combining the properties of homogeneous and heterogeneous catalysts. We have synthesized chiral SiO$_2$-based aerogels containing the S(+)phenylglycine fragment, which acts as a ligand for transition metal ions.

Strong copper and palladium complexes immobilized in the gel matrix were prepared. Aerogels were obtained by supercritical drying in isopropanol and CO$_2$. It was found that after supercritical drying in CO$_2$, the metal ion remained in the oxidation state (+2), and when dried in supercritical isopropanol, the reduction of palladium to the metal was observed, the particle size was 5-7 nm.

The obtained aerogels were used in catalytic experiments of liquid-phase hydrogenation of double C=C bonds of steroids and C=O bonds of acetophenone. It is worth noting that in all cases of hydrogenation, the predominance of one of the enantiomers was observed. In addition, palladium-containing aerogels were used in the Suzuki reaction, a typical cross-coupling reaction catalyzed by Pd(0) compounds. It has been found that the use of an aerogel-based Pd catalyst leads to a quantitative yield of the substituted diphenyl.

A financial support from the Russian Foundation for Basic Research (Grant 16-29-10736) is greatly acknowledged.
THE SUPERCritical CO₂ TREATMENT FOR THE REDUCTION OF CYTOTOXICITY OF GLUTARALDEHYDE – STABILIZED BIOPOLYMER MATRIX

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Abstract

The increase in biostability of medical products/materials based on proteins and their derivatives, including resorbable matrices for tissue engineering and regenerative medicine, is usually achieved mainly by cross-linking with glutaraldehyde (GA). One of the serious drawbacks of GA-stabilized products is their cytotoxicity due to trace amounts of GA. Finding ways to reduce the cytotoxicity of GA-fixated medical products continues to be an urgent task.

The aim of this work was to prove the efficiency of using supercritical CO₂ (sc-CO₂) in order to reduce the cytotoxicity of GA-treated composite porous tubular biopolymer (CPTB) matrices for tissue-engineered small-diameter blood vessels.

Materials and methods. Samples of CPTB matrices with a diameter of 3mm and 4 mm were obtained by electrospinning from poly(hydroxybutyrate-co-hydroxyvalerate) (PHBV) and gelatin solution (1:2 v/v) in hexafluoroisopropanol. The matrix structure was stabilized by treatment with GA vapor for 48 h. The treatment of CPTB matrices in the sc-CO₂ atmosphere was performed at a pressure of 150-300 bar, T = 35 °C at a flow rate of sc-CO₂ of 2.5 ± 0.5 ml/min for 8-24 h usingRESS-SAS equipment (Waters Corporation, USA). Ethanol (96%) at a concentration of 5-10% was used as a polarity modifier. Cytotoxicity of CPTB matrix fragments in vitro was evaluated on the culture of L929 mouse fibroblasts according to international standard ISO 10993-5 [1]. The proliferative activity of fibroblasts after direct contact with fragments of CPTB matrices was studied using the PrestoBlue™
Cell Viability Reagent (Invitrogen™, USA) on a microplate reader (Spark 10M, Tecan, Austria). Cultural polystyrene (CP) was selected as negative (noncytotoxic) control.

Results and discussion. Small-diameter CPTB matrices, produced from PHBV+gelatin solution (1:2 v/v), additionally stabilized by treatment with GA vapor for 48 h, had characteristics that were the closest to those of a native blood vessel of the same diameter in terms of surface structure, Young's modulus, and resorption rate [2]. The cross-linking of CPTB matrices with GA vapor for 48 h caused an increase in the cytotoxicity of the samples to “moderate” (32.9 ± 1.3% of proliferating cells compared to the number of proliferating cells in the negative control), which is unacceptable according to the requirements of international standard ISO 10993-5 [1]. Non-GA-stabilized CPTB matrices were not cytotoxic (96.9 ± 2.8% of proliferating cells) [2]. Treatment of CPTB matrix samples with sc-CO₂ for 8 h reduced their cytotoxicity to “mild” (68.6 ± 0.5% of proliferating cells). An increase in the sc-CO₂ treatment time to 24 h resulted in a decrease in cytotoxicity of CPTB matrix samples to “slight” which was accompanied by an increase in the proliferative activity of L929 mouse fibroblasts compared to the negative control from 68.6 ± 0.5 to 79.4 ± 0.4%, respectively. The addition of polarity modifier resulted in the absence of the CPTB matrix cytotoxic effect; even a weak negative cell reaction to a direct contact with the GA-stabilized sample was not observed.

Conclusion. Thus, the treatment of CPTB matrices consisting of a mixture of PHBV+gelatin (1:2 v/v), stabilized with GA vapor for 48 h, with sc-CO₂ for 8 h and 24 h, leads to a cytotoxicity decrease to the level permitted by International Standard ISO 10993-5, and the addition of polarity modifier reduces cytotoxicity to the degree of 0 - the absence of a cytotoxic effect.

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There are two factors affecting the kinetics of the reaction in sub- and supercritical water. They are high temperature and high diffusion coefficient [1]. This causes these reactions to proceed at very high speeds, and it is difficult to isolate the limiting stage. Would it be either the rate of chemical transformation itself, or the rate at which the reactants are supplied and the reaction products are withdrawn?

In our researcher we dealt with water oxidation processes of inorganic (metallic aluminum) and polymeric (natural polysaccharides, lignin and synthetic styrene-butadiene resins) substances. In all cases, the solid-phase reagent is pre-dispersed to a particle size of <100 μm, which was determined mainly by technical reasons, namely, the passage of particles through the nozzles of the feed of the initial suspension into the reactor and the stable operation of the injection pump.

The synthesis of aluminum hydroxide (boehmite) $\text{AlOOH}$ from metallic aluminum was carried out under subcritical conditions ($T = 330–350 \, ^{\circ}\text{C}, P = 15-17 \, \text{MPa}$). The influence of technological parameters, type of powder, alkali additives was investigated. With a residence time in the reactor of 60-100 seconds, the micron-sized aluminum particles completely transform into nanostructured boehmite with a crystal size of about 50 nm, which is a valuable product for many industrial applications. [2].

The product of the reaction is also gaseous hydrogen and a highenthalpy vapor-gas mixture. The resulting balance ratios are as follows: 2.2 kg of boehmite and 0.11 kg of hydrogen are produced per 1 kg of aluminum metal and 16 MJ of heat is released [3].

The complete oxidation of solid-phase organic substances was carried out at supercritical parameters ($T = 450-600 \, ^{\circ}\text{C}, P = 25-30 \, \text{MPa}$) with an oxidizer-oxygen of air or hydrogen peroxide. The substances that have been oxidized were spent ion
exchange resin, peat, husk of buckwheat, rice and sunflower, wood flour [4]. During the time spent in the reactor 80-160 seconds, complete oxidation of organic substances to the level of chemical oxygen consumption in the condensate of 50-150 mgO_2/l took place. Oxygen consumption was 120-150% of stoichiometric. On the basis of the conducted thermal calculations, the boundary contents of organic substances in the initial suspension are determined, above which the oxidation process becomes energy self-sustaining. For plant waste, this amounts to 20-25%. To reduce the content of solid waste, improve the technological properties of the suspension and provide a self-sustaining regime can be through the use of liquid organic waste as a dispersion medium, which allows both solid and liquid waste to be processed.

It is shown that the oxidation of suspended organic matter in a supercritical aqueous medium occurs with the formation of a high-enthalpy gas-vapor mixture, which can serve as a working fluid for the generation of electrical and thermal energy. This opens up the prospect of creating a new technology for utilizing solid organic-containing wastes at autonomous cogeneration ecological-energy complexes for settlements and industrial enterprises.

The work was carried out with the financial support of the Ministry of Education and Science of the Russian Federation on Subsidy Grant Agreements No. 14.607.21.0126 dated 10/27/2015 (Unique Identifier of the Agreement RFMEFI60715X0126) and No. 14.613.21.0004 dated August 22, 2014 (Unique Project Identifier RFMEFI61314X0004).

**Literature:**


SOLUBILITY OF ANTRACENE IN CLEAN AND MODIFIED SUPERCRITICAL CARBON DIOXIDE

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Recently, searches are underway for new ways to regenerate catalysts that are implemented in non-aggressive, inert media with minimal energy consumption. Such methods include supercritical fluid extraction (SCFE) regeneration, which is one of the promising innovative scientific and technological areas [1].

The main problem of the SCFE process is insufficient solubility of the solubility, which deactivates the catalyst of compounds in SCF media of a chemical nature. The results of the analysis of the composition of catalyst-deactivating compounds (coke) show that the characteristics of coke deposits on catalysts depend on the conditions of formation and can vary within wide limits in chemical composition, structure, dispersion and distribution on the catalytic surface [2]. Among the products of coke deposits, naphthalene, anthracene, etc. can be distinguished. In this connection, anthracene was chosen as the object of the solubility study.

The solubility measurements were carried out by the dynamic method on the original experimental device protected by the RF patent [3].

Experimental measurements of the solubility of anthracene in pure SC-CO$_2$ were carried out with isotherms of 423 K, 435 K, 448 K in the pressure range of 9.6 ÷ 22 MPa.

In addition, the solubility of anthracene was described using the Peng-Robinson equation of state [4, 5].

Comparison of experimental measurement values and descriptions of anthracene solubility, presented in fig. 1, shows that the standard deviation of the description results from the experimental data in the investigated pressure range on the 423 K, 435 K, 448 K isotherms does not exceed 6.48%.
Increased pressure and temperature have a positive effect on the dissolving ability of SC-CO$_2$.

In order to increase the dissolving power of supercritical carbon dioxide, a search for co-solvents of various nature (acetone, ethanol, hexane, etc.) was conducted. Studies have shown that hexane and ethanol are more effective modifiers. In this regard, the effect of the concentration of these cosolvents on the dissolving ability was analyzed. The content in the solvent 2% of the mass. hexane or ethanol had a maximum effect than their other concentration. The results of anthracene solubility in SC-CO$_2$ modified with hexane and ethanol are clearly shown in Fig.

Modification of SC-CO$_2$ had a positive effect on the solubility of anthracene. So with the maximum research pressure (20 MPa) using ethanol and hexane as a CO-solvent, the solubility of anthracene increased by 56% and 76%, respectively. The use of modifiers made it possible to increase the solubility of anthracene using ethanol and hexane by 56% and 76%, respectively.

*The work was done with the financial support of the Russian Foundation for Basic Research and the Government of the Republic of Tatarstan within the framework of the research project No. 18-48-160013.*

**Literature**


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Earlier in [1] the process of regeneration of the kerosene hydrotreating catalyst DN-3531 (Criterion Catalyst and technology) provided by the TAIF-NK oil refining association was described. The catalyst is aluminum oxide granules with nickel, molybdenum and cobalt oxides deposited on them. The metal content in the initial catalyst is: Co – 4.0 % mass, Ni – 3.0 % mass, Mo – 13.0 % mass. In [1] it was shown, that when using dimethylsulfoxide (DMSO) as a co-solvent, the activity of the regenerated catalyst practically does not change in comparison with the initial sample. Additional study revealed in this case that the removal of active metals from the surface of the catalyst takes place. In this regard, the aim of this work was to study the solubility of one of the active metals of the catalyst DN-3532 – nickel oxide – in pure and modified supercritical carbon dioxide. As the modifier we used DMSO. The solubility study was carried out on the plant described in works [2, 3] in accordance with the method described in these works.

Nickel oxide was found to be insoluble in pure SC CO$_2$. At the same time, under the pressure of SC CO$_2$, the dissolution of Nickel oxide in DMSO occurs and a complex compound $[\text{Ni(DMSO)}_6]^{2+}$, is formed. This complex in turn dissolves into SC CO$_2$.

The results of the solubility study are shown in Fig. 1. It presents the solubility as a change in the mass of the nickel oxide sample, referred to the mass passed through the CO$_2$ sample. In fact, the solubility obtained on the 383 K isotherm is slightly higher than the value obtained in the recalculation of the data from work [17]. In our opinion, this is because a whole bunch of substances is extracted from the surface of the catalyst, whereas in this study only nickel oxide is found in the cell.
The obtained result is of interest from the point of view of the existing problems of utilization of hydrotreatment catalysts and requires in-depth study in the future.

*The work was supported by RFBR and the Government of the Republic of Tatarstan in the framework of the scientific project № 18-48-160013.*

![Graph showing solubility of Nickel oxide in SC CO₂ modified with 5% mass. DMSO in comparison with data on nio removal from the surface of the catalyst on isotherms: 1 – 328 K, 2 – 343 K, 3 – 383 K, 4 – data from work [17], Table. 1 (383 K)](image)

**Fig. 1.** The solubility of Nickel oxide in SC CO₂ modified with 5% mass. DMSO in comparison with data on nio removal from the surface of the catalyst on isotherms: 1 – 328 K, 2 – 343 K, 3 – 383 K, 4 – data from work [17], Table. 1 (383 K)

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Research of thermodynamic properties of 1-propanol–n-hexane system in supercritical state is very important for design of adequate models of interaction potentials between polar and nonpolar substances of different homological rows. And with it accurate data on $p, \rho, T$-relations of 1-propanol–n-hexane system in the wide diapason of parameters of state is a great interest of development of solution theory and as a unique solvent for supercritical fluid technologies.

By using the method of free ballast constant volume piezometer new accurate values of $p, T$ and $p, \rho, T$-relations are obtained for 1-propanol–n-hexane binary mixtures ($x=0.2$, 0.5, 0.8 and 0.9 mole fractions of n-hexane) in the range of temperatures (373.15-573.15 K), densities (15-660 kg/m$^3$) and pressures up to 50 MPa in two-phase, one-phase (liquid–gas), critical and supercritical regions of state parameters (fig.1). By using isochoric $p$-$T$ break points the values of the liquid→gas phase transition (equilibrium) parameters are determined (fig.2).

![Fig.1. Isochores (1-30) of p-T dependences of 1-propanol–n-hexane ternary mixtures ($x=0.5$ mole fractions). LP–liquid phase, GP–gas phase, SCL–supercritical liquid, SCG–supercritical gas](image1)

![Fig.2. p,$\rho$,T-diagram of phase coexistence curves and their projections of 1-propanol, n-hexane and their mixtures ($x=0.2$ (1), 0.5 (2), 0.8 (3) and 0.9 (4) mole fractions of n-hexane](image2)
It is experimentally found out that phase diagrams of binary and ternary mixtures are similar to phase diagrams of individual fluid, i.e. researched systems may be considered as homogeneous.

The dependence of pressure of 1-propanol–n-hexane binary mixtures from temperature and composition of mixtures along the equilibrium phase curve is described by three-parameter polynomial equation represented by expansion of the compressibility factor \( Z = p/RT \rho \) into a power series of reduced density \( \rho \), reduced temperature \( \tau = T/T_{cr} \) and composition \( x \):

\[
Z = p/RT\rho_m = 1 + \sum_{i=1}^{m} \sum_{j=0}^{n} \sum_{k=0}^{s} a_{ijk} \omega^j \cdot x^k / \tau^i
\]

and

\[
p = RT\rho_m \left[ 1 + \sum_{i=1}^{m} \sum_{j=0}^{n} \sum_{k=0}^{s} a_{ijk} \omega^j \cdot x^k / \tau^i \right].
\]

The average relative error of calculated values of pressure from experimental ones less than 1 %.

By graph analytical method with a glance of scaling behavior, parameters of critical state \((p_{cr}, \rho_{cr}, T_{cr})\) are determined depending on composition \(x\) of system (fig.3). These values are fit well with literature data [1-4].

Fig.3. Dependence of critical temperature (a), critical pressure (b) and critical density (c) from composition of 1-propanol–n-hexane system. X – [1]; ○ – [2]; △ – [3]; □ – [4].

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using PC-SAFT EoS // The Journal of Supercritical Fluids. 2012. V.71. P. 26-44

By the method of free ballast constant volume piezometer new accurate values of
\( p, T, x \) and \( p, p, T, x \)-relations are obtained for n-hexane–water binary mixtures (\( x=0.2, 0.5, 0.8 \) and 0.9 mole fractions of n-hexane) in the range of temperatures (323.15-648.15 K), densities (55-570 kg/m\(^3\)), pressures from 0.1 to 40 MPa and for different values of composition (\( x \)) in three-phase, two-phase, one-phase (liquid–gas), critical and supercritical regions of state parameters.

By using isochoric P-T break points the values of the \( L_1-L_2\rightarrow G\leftrightarrow L_1-L_2 \) and \( L_1-L_2\leftrightarrow SCF \) phase transition (equilibrium) parameters are determined (table).

<table>
<thead>
<tr>
<th>( x, ) m.fr.</th>
<th>( T, ) K</th>
<th>( p, ) MPa</th>
<th>( \rho, ) kg/m(^3)</th>
<th>( x, ) m.fr.</th>
<th>( T, ) K</th>
<th>( p, ) MPa</th>
<th>( \rho, ) kg/m(^3)</th>
<th>( x, ) m.fr.</th>
<th>( T, ) K</th>
<th>( p, ) MPa</th>
<th>( \rho, ) kg/m(^3)</th>
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<td>0.190</td>
<td>384.15</td>
<td>0.532</td>
<td>572.75</td>
<td>0.219</td>
<td>435.85</td>
<td>1.662</td>
<td>505.90</td>
<td>0.219</td>
<td>453.15</td>
<td>39.496</td>
<td>502.67</td>
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<td>0.233</td>
<td>418.25</td>
<td>1.149</td>
<td>532.12</td>
<td>0.216</td>
<td>471.76</td>
<td>2.438</td>
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<td>0.216</td>
<td>534.15</td>
<td>25.685</td>
<td>469.61</td>
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<td>0.221</td>
<td>472.15</td>
<td>3.375</td>
<td>430.31</td>
<td>0.221</td>
<td>523.55</td>
<td>15.411</td>
<td>429.08</td>
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<td>504.95</td>
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<td>4.118</td>
<td>399.99</td>
<td>0.237</td>
<td>523.15</td>
<td>12.091</td>
<td>399.11</td>
<td>0.311</td>
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<td>360.40</td>
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<td>331.15</td>
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<td>7.234</td>
<td>147.71</td>
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</table>

By using experimental data of \( p, p, T, x \)-relations of gas, nearcritical and supercritical regions values of compressibility factor \( Z = p/RT\rho \) described by three-parameter
polynomial equation

\[ Z = \frac{p}{RT\rho_m} = 1 + \sum_{i=1}^{m} \sum_{j=0}^{n} \sum_{k=0}^{s} a_{ijk} x^i \cdot x^j / \tau^k \]

and

\[ p = RT\rho_m \left[ 1 + \sum_{i=1}^{m} \sum_{j=0}^{n} \sum_{k=0}^{s} a_{ijk} x^i \cdot x^j / \tau^k \right]. \]

The average relative error of calculated values of pressure from experimental ones less than 3 %.

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